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*Mrs. Morris Loeb*

*273. Madison Avenue*



**THE SCIENTIFIC WORK  
OF  
MORRIS LOEB**







Wm. L. Koch



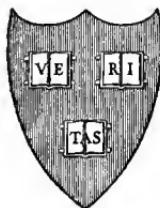


THE SCIENTIFIC WORK  
OF  
**MORRIS LOEB**

FORMERLY PROFESSOR OF CHEMISTRY AND  
DIRECTOR OF THE HAVEMEYER CHEMICAL LABORATORY  
AT NEW YORK UNIVERSITY

EDITED BY  
**THEODORE W. RICHARDS**

PROFESSOR OF CHEMISTRY AND DIRECTOR OF  
THE WOLCOTT GIBBS MEMORIAL LABORATORY  
AT HARVARD UNIVERSITY



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## PREFACE

THIS volume is published as a memorial to Morris Loeb, a man of rare gifts who was called in his prime from his many-sided activities. The book will serve to make more accessible the thoughtful and suggestive writings of one of the American pioneers of the new physical chemistry.

All the publications of the late Professor Loeb bearing upon scientific topics have here been brought together, except a few brief reviews in Italian possessing only transient interest; and there have been added such parts of several essays found in manuscript as he might have been willing to have printed. The collected papers have been divided into two groups; the first includes those of a general character (such as essays, lectures, and reviews), and the second those recording the results of his original experimental researches, which are more technical in their nature and less generally comprehensible. This division into two groups was made in order that essays having general interest should not be lost to the average reader by being hidden among scientific papers beyond his comprehension.

In each group the papers have been arranged in chronological order. Of those found in manuscript, parts of three discussions of the same subject have been welded together so as to make one consistent essay and placed at the beginning of the first group under the title "The Fundamental Ideas of Physical Chemistry." The first part of this essay was evidently given as the introductory lecture of a course on physical chemistry at Clark University in 1889. Each of the three papers was fragmentary; but fortunately the gaps

## PREFACE

occurred in different places, so that it was possible to construct almost entirely in the author's own words a fairly consistent whole. Although these fragments were not deemed worthy of publication by their author, and although doubtless he would have preferred to revise them before printing, it has seemed worth while to publish them because they formed one of the very first presentations of the new physical chemistry on this side of the Atlantic.

The popular address on "Atoms and Molecules" also was found in manuscript, and like the preceding essay, has had incorporated into it several scattered paragraphs upon the same subject from other incomplete notes. Thus it is hoped that all of his written work on this subject that is worthy of printing has been preserved in readable form.

Another paper printed for the first time is that on Sir Isaac Newton, which is of interest in showing the author's appreciation of the value of abstract scientific research.

The only other important paper found in manuscript (placed under the title "Chemistry and Civilization," at the end of the first group of papers) was intended by Professor Loeb to be the introduction to a proposed comprehensive book upon the usefulness of the science in its widest sense. Upon this book he was working at the time of his death; and one cannot but poignantly regret, after reading the introductory chapter, that the completion of the project was denied him.

Two of the researches included in the second group were published both in German and in English; in these cases both versions are reprinted, because the translations are evidently the author's work, and differ in several details from the originals.

In each of the scientific articles included in the second part of the book, the page numbers of the original publication are inserted in brackets at the proper places, to show

where each page begins and ends. This is done for the convenience of commentators wishing to refer to the original articles. All the papers have been reprinted essentially in the form used by the author. The historical advantage of this practice is obvious; and although usage in nomenclature, notation, and spelling has somewhat changed during twenty-five years, the older forms cannot in any of the present instances give rise to misunderstanding.

After the scientific contributions, Professor Loeb's laboratory manual of experiments for the elementary course in inorganic chemistry at New York University is printed as an appendix, together with the description of a brief series of experiments upon the speed of reactions. These are included not only for the sake of completeness, but also because they may be suggestive to others confronted with the interesting but difficult task of giving elementary instruction.

A complete chronological list of all the separate essays is given at the end of the volume, with the references to the original sources; and an index of names completes the book.

Other manuscripts and notebooks found in his laboratories contained much that was almost ready for publication, but probably nothing more that he himself would have considered as ready to appear in print. The preliminary search among these papers was conducted at the request of his family by Professor Charles Baskerville, of the College of the City of New York, and Mr. D. D. Berolzheimer, a former student of Professor Loeb's and the librarian of The Chemists' Club; thanks are due to both for their valuable assistance in making a preliminary selection and arrangement of the material, and to the latter, as well as to Professor G. S. Forbes, for their help in reading the proofs. To Professors Charles Loring Jackson, Elmer P. Kohler and Gregory P. Baxter also the editor is grateful for advice.

T. W. R.



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## THE LIFE AND CHARACTER OF MORRIS LOEB

IN the untimely death of Morris Loeb our country lost a man of rare quality. To serve mankind was the ideal of his life, and loyalty was his guide in the fulfillment of this service; few men in so short a span of years have been able to express so largely their desire by deeds. His helpful acts and liberal benefactions were modestly carried out; they were perhaps hardly appreciated in their fullness during his lifetime by any except those who came nearest to him. As an ameliorator of the lot of the poor of New York he was in the front rank; at the same time he was a farseeing enthusiast in the cause of science, and one of the most faithful and generous graduates of Harvard University. His devotion to his Alma Mater makes it especially appropriate that this volume of his writings should appear under her auspices.

Among his various interests chemistry was foremost, although the responsibilities of a great fortune and its attendant demands prevented him from devoting as much time to research as he would have been glad to give. The study of his work as disclosed in the following pages will show a mental attitude unusually thoughtful and philosophic, alive to new ideas and yet wisely conservative. His conservatism was not of a reactionary type, because he was ever altruistic in his point of view. His constant aim was to support that which seemed to him likely to contribute, either through the advance of science or in any other way, to the good of mankind.

Morris Loeb was born fifty years ago at Cincinnati, Ohio, on May 23, 1863, the son of Solomon and Betty (Gallenberg) Loeb. His father was one of the founders of the great bank-

ing firm of Kuhn, Loeb and Company. While the boy was still young, his parents removed to New York, and his primary education took place at the school of Dr. Julius Sachs in that city. In the autumn of 1879 he entered Harvard University and graduated there with the degree of Bachelor of Arts in 1883.

He was an able and conscientious student in college. His interest centred at first in the older discipline of the classics, but it changed to the newer discipline of chemistry and physics as his college life advanced. His experience under Charles Loring Jackson in "Chemistry 1" during his Freshman year seems to have awakened that love of science which, fostered as it was by Wolcott Gibbs in his later years, determined his life work. As an undergraduate he received a "Detur" or prize for high scholarship, and at graduation he attained his degree "Magna cum Laude" on his general average, as well as with "Honorable Mention" in chemistry and English composition. His best chemical work in college was done in the field of organic chemistry under Henry Barker Hill, and this interest was continued in his studies immediately afterwards in Germany, as is evidenced in his first two scientific papers.

During the period of his stay in Berlin, where he studied under August Wilhelm von Hofmann and received the degree of Ph.D. in 1887, the new interest in physical chemistry had risen above the intellectual horizon of Germany, and Loeb's farsighted intelligence at once grasped the significance of the coming science. The winter after he received his degree, he entered the University of Heidelberg for the study of physical chemistry, and during the following summer he attended the University of Leipzig, working under the brilliant new leader, Wilhelm Ostwald, and in collaboration with his able assistant, Walther Nernst.

In the autumn of 1888 Loeb returned to America; he was now so thoroughly imbued with a passionate love for science that the urgent appeal of the brilliant position in banking which was open to him was not heeded. Instead of turning towards finance he entered upon a voluntary private assistantship under Wolcott Gibbs, who had recently retired from his Rumford Professorship in Harvard University and as Professor Emeritus had established a private chemical laboratory near his house at Newport, Rhode Island. Their mutual affection, which had begun years before when both were at Harvard, was intensified by this close association; and it is typical of the characteristic faithfulness of Loeb's nature that nearly a quarter of a century afterward he should have suggested the naming of a new laboratory for research, founded at Harvard by him and his brother James Loeb (of the class of 1888), in honor of Gibbs.

In 1889 the young physical chemist was appointed to a docentship in Clark University. His opening lecture there was probably the essay given first among the papers included in this volume; he never published it himself, but the manuscript remains in his own handwriting. This lecture shows his intelligent appreciation of the main problems of the new physical chemistry and their great importance. He was indeed one of the pioneers in America in this new field of science, and his influence was far-reaching.

In 1891 he was elected to a professorship of chemistry in New York University, and four years afterwards became director of the chemical laboratory there, an office which he held for eleven years. His resignation in 1906 was due not to any weakening of his interest in chemistry, but rather to the pressure of countless other demands upon his time, which made the routine of such a position almost if not quite impossible.

Much of his energy was given to a number of charitable

organizations; for his keen sympathy with human suffering caused him to be ever responsive to the needs of the unfortunate. His charitable work, like his generous activity in other directions, was by no means restricted to his own race, although he was of course especially devoted to associations which had as their object the improvement of the lot of the great mass of Hebrew poor in New York. He was president of the United Jewish Charities Building, a member of the American Jewish Committee, a trustee of the Jewish Theological Seminary of America, and was at one time president of the Jewish Agricultural and Industrial Aid Society. He was, moreover, president and one of the founders of the Solomon and Betty Loeb Home for Convalescents, erected in memory of his parents.

Another enterprise demanding much of his time was The Chemists' Club of New York, the welfare of which he did much to promote. Here again he was characteristically earnest in his effort to help in every possible way those for whom he felt himself especially responsible. Twice he was vice-president and twice president of the club, and it was during his first presidency in 1909 that the idea of housing the club and its admirable library in a dignified building first took shape. He not only gave outright many things to the unique building which rose under his direction, but also was one of the chief stockholders in the enterprise. His generous bequest of all his holdings of stock in the building to the Chemists' Building Company for cancelation cannot but do much to fortify the future of the Club and help towards its permanent existence.

In 1908 he was appointed one of the committee of the Harvard Overseers to visit the Chemical Laboratory. As usual he entered very faithfully into this new responsibility and, unless in foreign lands, attended every meeting of the committee,

although such attendance involved on each occasion a trip to Boston. Besides making this sacrifice of time and energy in behalf of his beloved University, he bore always in mind the difficulties of the struggling Division of Chemistry, and frequent letters, often written in his own hand from remote countries, brought valuable suggestions to the department and attested his constant interest in its welfare and in the growth of his chosen branch of science at Harvard. As already stated, it was upon his initiative, through the generous gift of \$50,000 from his brother James Loeb and himself, that the Wolcott Gibbs Memorial Laboratory for research in physical and inorganic chemistry was founded at Harvard.

Largely through his interest and endeavor the Association of Harvard Chemists was formed, from among the alumni of the University; and his hospitality to this association during the Eighth International Congress of Applied Chemistry in 1912 will long be remembered by those who were fortunate enough to be his guests at that time.

His devotion to the Congress was characteristically strong. Since delegates from all over the world had been invited to this continent, he felt that Americans should take especial pains to make the meeting a success. Although he had only just returned from a long trip to South America, undertaken with the hope of stimulating interest in the undertaking, he threw himself with self-sacrificing enthusiasm into the work of preparing for the reception of the foreign guests in Washington and New York.

Besides being a member of the Congress (and an unusually helpful one), Professor Loeb was a fellow of the New York Academy of Sciences and of the American Association for the Advancement of Science, and a member of the American Chemical Society, the German Chemical Society, the American Electrochemical Society, and the New York Elec-

trical Association. He received the honorary degree of Doctor of Science from Union College in 1911.

During the twenty-nine years between his graduation and his death, Morris Loeb published thirty papers, reviews, and essays. Many of these depended upon experimental work carried out at the universities in Berlin, Heidelberg, Leipzig, Worcester, and New York, or in the private laboratories which he himself established, after his retirement from active teaching, in New York and on his beautiful country estate at Sea Bright, New Jersey. For the reasons already set forth, the extent and scope of his experimental researches were far less than he wished; but, even so, the work forms a sum total of which any one might be proud.

His investigations dealt with a wide variety of topics and showed a steadily increasing desire to penetrate further into the fundamental mysteries of the nature and mechanism of chemical reaction. To those not conversant with the subject it would be impossible here to explain the purport of these investigations, and to those familiar with its details the papers speak for themselves. No one can turn the pages without the conviction that this work was carried out with the earnest desire, which marks the sincere man of science, to discover the truth and nothing but the truth.

Morris Loeb's vivid interest in the advance of science did not preclude an intelligent appreciation of achievement in other fields of human activity. He was deeply interested in music and art, and was one of the founders and endowers of the Betty Loeb Musical Foundation. Himself a teacher for years, he was greatly interested in all educational causes. For several years he was a director of the Educational Alliance, and at the time of his death he was a member of the Board of Education of New York City and president of the Hebrew Technical Institute.

On April 3, 1895, he was married at Cincinnati, his native city, to Miss Eda Kuhn, who survives him. After more than seventeen years of devoted married life, he died on October 8, 1912, falling a victim to typhoid fever and double pneumonia. He was a martyr to his noble ideal of service; for one cannot but believe that the way for his fatal illness was paved by his over-exertion in welcoming at Washington the members of the International Congress. The interment in the family vault at Salem Fields, Cypress Hills, Long Island, took place in the presence of a sorrowing throng of men and women of many creeds and stations.

The esteem in which he was held is manifest in the many deeply appreciative resolutions now spread upon the records of the societies of which he was a member. From among these, two are quoted below, as typical of the general recognition of his worth.

At the meeting of the Trustees of The Chemists' Club on the day of his death, the following preamble and resolution, drawn up by Ellwood Hendrick, Clifford Richardson, and Walter E. Rowley, were adopted:—

“WHEREAS, Morris Loeb, the President of the Club, has been taken from us by death; and

“WHEREAS, he was the leading spirit in bringing to fulfillment ambitions and plans that had long been ours; and

“WHEREAS, he was always ready to shoulder burdens and to give help; and

“WHEREAS, he was a man of order, and of integrity, in mind and heart, sincere in scholarship, living without malice or scorn, speaking no evil, and generous in judgment; and

“WHEREAS, we were drawn to him by ties of deep and abiding affection; now, therefore, be it

“*Resolved*, that we make this minute of our poignant grief

at his passing, and that we cherish his memory as another of his great gifts to science and to humanity."

The following sentences, written by Marston T. Bogert, Charles F. Chandler, and William H. Nichols, and entered upon the minutes of the New York Section of the Society of Chemical Industry, express again the general appreciation of his life and character:—

"Morris Loeb, chemist, investigator, educator, upright and useful citizen, altruist, philanthropist, generous patron and benefactor of art, of sciences, and of all good works, ever ready to bear more than his share of the burdens of the community and always to be found on the side of righteousness, justice, and truth, lived his life of quiet power without arrogance or display. Always modest concerning his own distinguished career and many accomplishments, with charity towards all and unkind criticism of none, he was ever a courteous, genial, and polished gentleman of high ideals, whose chief aim and purpose was to be of assistance to his fellow-men, and who realized to the full that the highest reward of service is the privilege of having been of service.

"Now that the temporary scaffolding of life has fallen away, the true nobility of his character stands clearly revealed in all its commanding beauty and dignity, an imperishable monument of a life's work well done and a worthy inspiration to others. Such manhood is the real glory to any country. The world is the better for his having lived in it, and we are the better for having known him."

Any statement of the good wrought by this ardent worker in the cause of science regarded as an agent for human advancement would be incomplete without allusion to several of the provisions of his will. By it he assured, as has been already said, the permanence of The Chemists' Club as a

centre of chemical influence in the country; he provided for the establishment of a museum of rare and typical substances to be maintained by the American Chemical Society; and, most important of all, he bequeathed a fund of \$500,000 to be used eventually by Harvard University for the furtherance of the sciences of chemistry and physics.

These provisions, like many of his earlier benefactions, will bear blessings far into the future; the fruit of his contributions to the welfare of humanity will multiply.

In Morris Loeb's life and character our country and Harvard University have a right to take deep pride. Upright, unselfish, generous, loyal, sincere, wise, and modest, he set a noble example; his memory is treasured by all who had the privilege of knowing him. When those too have left this earthly life, he will be kept in remembrance by his great gifts to science and to charity, and be honored by many generations in the years to come.

THEODORE W. RICHARDS.



**PART I**

**LECTURES, ADDRESSES, AND REVIEWS**



## THE FUNDAMENTAL IDEAS OF PHYSICAL CHEMISTRY<sup>1</sup>

IN commencing this course of lectures, whose subject-matter and title are avowedly new to the American student, I feel the need of giving some justification, of presenting some reason why I should seek to add one more round to the ladder of learning already so alarmingly long. To-day, the cry against specialization is increasingly raised; and we now and then hear voices wailing for the good old times, when an Admirable Crichton could boast of knowing something of all things knowable, and when a Pico della Mirandola could publish his readiness to dispute against all comers, "de omnibus rebus."

But wishing these times back will not recall them. Loosed from the leash of rhetoric and dogmatism, the pursuers of knowledge have spread in all directions over the field, each so eager on his own particular trail that he has no eye for the discoveries of his neighbor; he forgets, indeed, that there is need of keeping in touch to the right and left, lest important clues be passed unobserved. No wonder if the bewildered spectators should think that the whole pack has gone mad, and that the majority, at least, have been diverted, by their own self-sufficiency, from the noble quarry upon which they had been set. Nevertheless, we may already see a change in their methods: they are shaping their courses parallel to each other, they strive to keep abreast and neighbors instead of running apart; they carefully scan the ground between themselves, that nothing may lurk there unseen.

<sup>1</sup> Introductory lecture of a course probably given at Clark University in 1889.

To speak in more sober language, while it is still necessary for the advancement of knowledge that investigators should concentrate their energies on their particular fields of science, these various branches are now approaching so close together that one will aid the other, if properly directed. While, therefore, it would be preposterous to demand of the anatomist a full knowledge of astronomy, or to ask a geologist for his opinion of the various hypotheses concerning the structure of benzol, we may justly deride the man who confines himself so closely to his own particular hobby that he remains ignorant of those subjects which are neighboring links in the chain of knowledge, merely because he does not expect aid from them. Such men may be most skillful in delving for new facts, they may light upon discoveries which will make their names famous, fill their pockets, cover their breasts with decorations, and stuff their cabinets with diplomas. But the actual merit of incorporating these facts into the world's knowledge will belong to him who, with a wider view, will connect them with other isolated facts to form a harmonious whole.

Especially has our own science been unfortunate in producing hundreds of specialists of the narrowest order. The ever-increasing number of subjects which claim attention, the perplexing rapidity with which new views supersede older ones, the restriction which the work in the laboratory places upon our time, — these have all had a share in persuading chemists to confine their attention to a narrow field and to give scanty hearing to that which does not concern their own particular work. But, worse still, we have to contend with the opinion that chemistry is a *practical* science, that it is our chief glory to produce new compounds of unheard-of intricacy, that our recompense is to be sought in some discovery which will have a commercial value. Far be it

from me to detract from the merits of a Liebig, a Hofmann, a Horsford, a Deville; the discoveries by which they have enriched mankind are among the brightest ornaments of our science. But the brilliancy of their achievements has so dazzled the eyes of the world as to lead men into the danger of forgetting that the true duty of a science is the investigation of natural phenomena, and that the employment of known forces for the production of effects which, however novel and beautiful, depend merely on ingenious combinations, must soon bring chemistry to the level of an art. Too many chemists hurry in their studies toward the El Dorado of carbon synthesis, striving to obtain at the earliest moment tangible results in the shape of new substances, be they dyes, drugs, or merely triumphs of synthetical art. In this eager chase they rush heedlessly over the rich fields of stoichiometry, of inorganic chemistry, of analysis, of electrochemistry, of the problems of chemical affinity.

Like to the miners of '49 the specialist in organic chemistry has but one thought. Arrived at his diggings, he delves assiduously, and if favored by fortune and skill is rewarded with many a rich nugget. But if, resting awhile from his labors he decides to retrace his steps and revisit former scenes, he is astounded to find that lands passed by as cheerless and barren have been occupied by settlers, who with patience and care have cultivated and beautified them, and are now reaping wealth more lasting and productive than his own gold.

Let us, then, who have not staked our claims, travel more leisurely, tarrying here and there, surveying our fair inheritance and considering whether it be not our duty to turn aside from the main road,<sup>1</sup> in order that we may render fruitful that which would else be a noisome desert.

<sup>1</sup> In 1889 this "main road" was the study of synthetic organic chemistry.  
[Editor.]

Chemistry, as I have intimated, owes its great prominence, in popular estimation, to those material successes of the branch called organic chemistry, which have rapidly succeeded each other during the last thirty years. Their foundation was laid by that grand work of systematization, with which we find connected the most glorious names of modern chemistry, Liebig and Wöhler, Laurent and Gerhardt, Dumas, Hofmann, Wurtz, Williamson, Couper, Kekulé, and Cannizzaro. So extensive and intricate is this system, and yet so fruitful in all its ramifications, that it has well repaid the intense labor bestowed upon it by these men and the hosts of their pupils and successors. But we must not lose sight of the fact that, after the first successful generalizations, the work has been mainly deductive and not inductive. We have had an algebra devised for us with its own notation and its own processes of reasoning: it remains for us to combine these ingeniously, so that they may apply to the special problems with which we are confronted. Our success is so great, that it appears that the propositions upon which we started are axiomatic instead of hypothetical, and general instead of special; so that, when we have quoted one of them, we believe that we have stated the first principle to which any question can be referred. As a matter of fact, organic chemistry by itself only clears up the questions of composition and constitution and of change within the molecule. The interesting problems as to the nature of what we call atoms, the properties of the elements, the peculiar behavior of the molecules toward each other, and — grandest problem of physical science — the correlation of matter and energy, do not present themselves to the organic chemist. We shall have occasion to see how reluctant he is to accept other explanations than those given by his formulæ for phenomena which these formulæ seem incapable of explaining fully.

Turning now to inorganic chemistry, we find it completely overshadowed by its younger rival: its votaries are few and disheartened. I think that I do no injustice in asserting that, for most students, the mention of this study conveys no idea but that of laborious quantitative analysis for commercial and mineralogical purposes. That subdivision which corresponds more closely to organic chemistry, the description and natural history of the elements and their compounds, is generally taught chemical students at the very beginning of their course of study, and must naturally appear to be elementary and of least importance and interest. They may indeed also recollect dimly some few introductory lectures, given as a necessary evil and listened to with imperfect comprehension, about the atomic and molecular theories, the nature of reactions and the physical properties of compounds, but these also are for the most part hidden in the mists of the past.

Do not understand me as saying that all these subjects have not had skillful investigators during the last thirty years. This is by no means the case; we shall come across many revered names in the course of our review. The trouble is that their work has not received that attention from the whole community of chemists, which would make it as commonly known as are the achievements of organic synthesis, and place it upon its proper pedestal for public admiration. Why should we know less about silicon, iron, and sulphur, than we know about carbon, hydrogen, oxygen, and nitrogen? Why should we care more about the color, melting-point, and boiling-point of a compound than we do about its behavior towards other manifestations of energy beside light and heat? Above all, why should we confine ourselves to the internal constitution of molecules, when we should also concern ourselves with their behavior toward each other, with those mysteries

of affinity and reaction which cannot be explained by merely paraphrasing the phenomena? Not merely book-learning may be acquired by this knowledge; it continually furnishes us with new weapons for the further investigation of truth.

Gentlemen, the interest in general and physical chemistry is reawakening, and we may soon hope to see these studies as prominent as they were in the times of Humphry Davy and Gay-Lussac, of Berthollet and Dalton, of Berzelius and of Michael Faraday. I am thankful that this new university has granted me an opportunity of calling attention to them in our country; and I shall be happy indeed if I can augment in you the love for this branch of speculative philosophy, by pointing out some recent achievements and showing how much still remains to be done.

Confronted with the necessity of defining the scope of chemistry, I would say: *Chemistry is that branch of Physics which treats of the differentiation of matter.* Treading gingerly on the dangerous ground of metaphysics, we may recognize that there are four principles to which the educated mind refers natural phenomena, — four first causes, four categories, four systematic axes, — namely: energy, matter, space, and time. The practice of referring all outward impressions to *these* ultimate principles is undoubtedly a great advance over the assumption of the cruder “elements” of the Middle Ages, earth, air, fire, and water; but even energy, matter, space, and time are not by any means ideas to which we attach a definite, unalterable meaning. Their definition seems to vary in different minds and at different times in the same mind. Some prefer to consider time a mode of space, and others consider both time and space attributes of matter and energy, but not as independent essentials. All that we can say of energy and matter is that they *exist*, at least to our perceptions. We are apt to consider matter as some-

thing more tangible and *material* than energy, but this is because we confound substance with matter. In fact, we are no more acquainted with matter than with energy. We know matter by its reaction with energy, and energy by its reaction with matter. Since one thus defines and differentiates the other, we are moving in a vicious circle, and must pretty well despair of reaching, upon physical grounds, a perfect view of the real essence of either. Matter must, however, be defined for our purposes, and let us therefore frankly regard it as Aristotle did, the *ὕλη*, or stuff, from which the Universe is shaped as is the house from timber, or pottery from clay.

Whether this ultimate matter is homogeneous or not, we have no means of knowing, but our instinctive love of simplification leads us to suppose that it is homogeneous and one. This, however, is a purely hypothetical assumption. When we make an impartial study of fact, we find that by combining certain portions of matter with certain portions of energy, we obtain what is known as substance, and this may appear in infinitely different forms. It will seem odd to you that I should define substance as a combination of matter and energy, but a little reflection will show you that this view is quite admissible. All substances show certain qualities which are referable to energy, and may be considered as a combined phenomenon of matter and energy. Thus we are almost unable to imagine substance without the energy of gravitation, of motion, of chemical affinity.

Modern physics teaches us that energy is *one*, inasmuch as each form of energy is convertible into every other form, in certain definite quantitative ratios. The instinct of the alchemists told them that all matter was one, and each form was convertible into every other form. If this were the modern aim of chemistry, we should be obliged to confess that very little has been accomplished as yet. We have

reached a class of about sixty-five substances, which we have not yet been able to decompose or transform, and which we call the elements. True, many chemists believe that these elements are themselves composite, but whether this is so, and whether indeed the supposed substances of a more primitive order would be recognizable by chemical means, is a question which we are unable to answer. At present we shall assume that the chemist recognizes the existence of different substances arising from different relations between the hypothetical matter *par excellence* and the coördinate essence which we call energy.

In all this attempt to formulate the essential conditions of material existence, the tendency of our mind is toward a simplification of our standards of reference, — toward a lessening of the number of pigeon-holes into which new ideas must be put. We love to believe that the higher we ascend on the scale of causation, the smaller becomes the number of coördinate causes. Our experience appears to justify us in this reasoning, and so, as I have said, we have arranged for ourselves at that point where our experience appears to stop, the fiction of these four principles, space, time, matter, and energy. Let us not flatter ourselves, however, that this is an achievement of modern physics. The speculations of philosophers long ago led them to the same physical conceptions, and if Aristotle's elements appear grosser to us, it is because we have stripped off, as unessential, some of the accessory qualities with which he had clothed the mathematical skeleton. Struggle as we may, we cannot rid our own few principles of some quality in common and consequently ulterior: above all things we give them alike that vague, awesome attribute of *existence*: essences, let us call them, because they appear to us to be the ultimate things that exist, according to our mundane imagination. All that we tell ourselves is,

that we can ascribe all the phenomena which we see to the combination of these essential principles, of whose nature we know nothing, and which are, consequently, infinite to us. This does not preclude our singling out finite portions of these, so to speak, and defining them by each other.

We have seen that we are not justified in calling substance a manifestation of matter free of energy: it is so intimately connected with certain forces (such as gravitation) which are convertible into so-called manifestations of pure energy, that we cannot conceive of it as existing deprived of these, and yet remaining recognizable. But we may nevertheless class all substances together in one general class called matter.

Thus also, the various modes of energy — heat, motion, electricity, chemical affinity — are phenomena which we dare not ascribe to energy alone, for we cannot conceive them as separated from matter. We can, therefore, speak of their differentiation also, although we may picture the transcendental energy as one and homogeneous. Indeed, consciously or unconsciously, this distinction is made in the science of thermodynamics, which proposes to treat energy in its abstractest form. . . .

In view of these philosophical complications, I propose that we do not allow ourselves to be hampered by metaphysical notions as to the respective homogeneity of matter and energy, but that we accept frankly, at the outset, the appearance of substances and forces in various distinct forms. Physical research will show us that there exist between all these forms certain relations, about which it is our duty to procure definite ideas. If the advance of knowledge shall gratify our love of symmetry, by proving that the correlations of the various forms may be traced to the existence of a simpler set of relations, of a higher order, well and good! But

let us not allow our feelings to warp our judgment, or a priori reasoning to mislead our investigations.

Of the various properties by which we recognize substance, there are some which are necessary concomitants of the very existence of matter, — which appear to accompany matter so faithfully, that no particle can boast of holding much more than another. Among these we reckon *extent, impermeability, mobility, gravitation, inertia*. . . .

Then there are other properties which we do not hesitate to term accidental; they are so loosely connected with the substances that we do not recognize the substances as dissimilar on that account. They might more properly be applied to the differentiation of energy. Such properties are position, temperature, electrical or magnetic change. They, indeed, may appear on one body more than on the other; but exchange the proportionate quantities in the two bodies, as well as we may, and yet we shall not be likely to confound one body with the other. These are all transferable properties, the one body gaining what the other loses.

There are, however, yet other properties, more or less concerned with the foregoing, which two bodies may not possess in like degree, and which it is impossible for one body to convey to the other. Substances differ in their behavior toward the same form of energy or toward each other, in the distribution of their mass in space (specific gravity), in their effect upon our senses, and upon the animate organism in general. These properties cannot be transferred from one body to another; but one substance may modify by its presence the properties of another. Such are the properties which really distinguish the different forms of matter, and it is with these that chemistry has to do.

The indivisible unit for the chemist is to be found in the homogeneous substance; beyond this he must confess that

he cannot go. As soon as he has found something in which he can detect nothing heterogeneous, which he is unable by any known means to divide, he stops at what he calls the elementary atom.

You will notice that this is by no means a positive definition by which we deny to our imagination the right of subdividing our atom or of dissociating our element. We merely ask for better proof than that of instinct, before we allow the inferences that are to be drawn from such a further subdivision to affect our treatment of the subject. The testimony which we present in favor of the homogeneity of our ultimate element is purely negative: we have found no heterogeneity. For example, we take this piece of rock; to the geologist, it presents itself as a unit, granite. The lithologist sees in it a composite mass of quartz, feldspar, and mica, which again are individuals for his eye. But for the chemist, feldspar is highly complex: he can isolate from it, silicon, oxygen, potassium, aluminium, magnesium, iron, and possibly other elements. No means have yet been devised so subtle as to subdivide these elementary substances.

Recognizing such as our simple substances, we find that each has certain properties of its own, which serve to distinguish it from the rest, and which cannot be transferred from it to one of its fellows. The ancient and mediæval alchemists regarded these elements as composites, containing in different proportions those principles of Aristotle to which we have already referred. To them, therefore, it seemed perfectly logical, that by addition or subtraction of some quality-bearing principle, one metal could be converted into another. It is only because we have, by carefully conducted experiments, found the metals to be homogeneous, toward all the agencies which we know,— that we have come to another conclusion, and ridicule the idea of their mutation.

Their reasoning appeared to them to be as logical as ours is, when we propose transforming the sap of the pine into the essence of vanilla, or of converting clay into the true ruby.

As I have said, we recognize upwards of sixty-five elements, but we rarely see any of these pure. Terrestrial objects must, then, be made up of combinations of these elements. In order to study them in the pure state, they must usually be separated from each other; and they are worthy of very careful study.<sup>1</sup> . . .

You are aware of the Periodic Law of Newlands, Lothar Meyer, and Mendeléeff, which traces such remarkable relations between the various properties of the elementary substances and the relative masses of their imaginary atoms. Attempts to connect this law with the idea that the elements are compounds in a chemical sense are abortive. I believe that the law can be more readily traced to the relation of the quantities in which our fundamental ideas of matter, energy, and space are associated for each element. The atoms of the elements have undoubtedly different densities. That is to say, our knowledge of the sizes of the atoms, limited though it be, does not allow us to suppose that an oxygen atom occupies sixteen times the volume which a hydrogen atom requires, although this is the ratio of the masses of these two kinds of atoms. For the same amount of space there seems to be more matter in the oxygen atom than in the hydrogen atom; we may assume that similar relations exist in other cases with regard to energy and matter. For each element we should have to assume new quantities of matter, space, and energy; and the ratios of every one of the three with respect to each other would vary. We might suppose, however, that for a series of elements the ratio of two of the fundamental quantities

<sup>1</sup> The lecture notes on physical chemistry here became fragmentary. The following six pages were taken from two summaries evidently prepared for addresses on other occasions. [EDITOR.]

remained fixed, but their ratio toward the third varied; in such cases we might expect marked similarity in their properties, as compared with those cases where all the ratios varied. Such reasoning, carried out more fully, might explain the peculiarities of the Periodic Law, even though this does not necessarily imply that no other explanation is possible.

Even if we do not altogether understand the relations between the elements, our chemical theory concerning the nature of these elementary substances is very simple. Assuming the elements to exist, each element is represented by one set of extremely small indivisible atoms, the atoms of the same element being exactly alike in all respects. They are independent bodies exerting upon other atoms an attraction which varies according to their nature. . . .

These atoms are supposed to unite into small clusters that we call molecules, and consider as the smallest independent bodies that have the properties of ordinary tangible substances. They remind us strongly of planetary systems, like our solar systems, because they execute their own movements quite independently of the movements of their constituent atoms. The molecules present comparatively easy problems to the theorist; their own motions seem to be simple and their mutual attractions are at least in part those of gravitation. The so-called "kinetic theory of gases" explains all phenomena of the gaseous state very readily by assuming that molecules move in straight lines until they hit an obstacle and are then reflected. If molecules come very close to one another, their relative attraction becomes much greater than that which corresponds to gravitation. I think it fair to assume that then their more complex chemical attractions come into play.

Thus our chemical philosophy becomes an attempt to interpret the actions of these imaginary atoms constituting matter

under the play of the various forms of energy which pertain to them; and these actions must be supposed to take place in tridimensional space during perceptible time.

Let us turn now to the consideration of energy. We talk of kinetic energy, or energy performing work, and of potential energy, or energy which is capable of performing work, but not yet doing so. In the case of the mechanical energy of motion, the potential form involves change in time but not in other obvious ways. It keeps on existing in the shape of a tendency to move, attraction or the like, while the kinetic form involves both a change in respect to time and to the directions of space. We recognize this in the word speed, or velocity, which expresses the distance traversed in comparison with the amount of time consumed. I think this energy of motion to be the easiest to conceive, and consequently the most natural to imagine as at the bottom of all phenomena of energy. Certain it is that physicists are finding more and more reason to believe that all the various forms of energy are really only manifestations of different sorts of direct motion.

For example, we find that what we know as heat or light may be simply interpreted as a manifestation of the motions of the molecules. If we heat a substance, its molecules may be supposed to move more rapidly in straight lines and vibrate or oscillate more rapidly. The oscillations they are able to impart to neighboring particles that may be incapacitated from directly taking up the rectilinear motions. If these motions or oscillations are very rapid, they affect our sense of temperature. They may partly belong to the molecule as a whole, partly to its atoms.

All sorts of molecules may be supposed to receive the straight motions in equal degree; but each molecule seems to respond only to certain kinds of oscillations. So we can throw a set

of bells an equal distance at the same speed; but each bell has its own rates of vibration, its tones and over-tones. You know that in light and heat vibrations, the colors of the spectroscope are due to the preference which molecules exhibit for certain rates of vibration. . . .

What now are the forms of energy concerned in causing chemical action? Until recently the chemist has dealt with static chemistry, — that is, the science in which the properties of quiescent substances are discussed, — rather than with the branch of knowledge which discusses the mechanism of chemical change. Whenever affinity is treated as a specific inherent property of the atoms, we naturally adopt the old-fashioned views first enunciated by Bergmann more than a century ago, that elements unite according to their specific affinity for each other. If two substances are presented to a third which would combine with either of them, it was supposed to take up the one for which it had the greater affinity, leaving the other uncombined. This doctrine of elective affinities is a comfortable, but unfortunately an incomplete one. It represents only one side of the question.

If we continue building upon the kinetic theory discussed above, a more complicated process is to be expected. As a matter of fact we find that substances act upon each other not only according to their mutual affinity, but are also influenced by such conditions as their relative quantities in a given space, their temperature, etc. To illustrate the former of these two circumstances, suppose a mixture of equal masses of A and B, which do not act upon each other, to be presented to C, with which both can react, but A more readily than B. A and C will unite, but not to the exclusion of B; there will be a partition of C between A and B, in which A, the more active, gets the greater share of C. When, however, the quantity of B originally present is increased, more of

C will combine with B than would originally combine with it. This is due to the fact that chemical action is due to exchange of atoms when molecules meet. In spite of some reluctance to combine between B and C, the greater number of molecules of B present causes more frequent meetings between B and C atoms than between A and C atoms. Throughout chemical reactions it is found to be true that the ultimate result depends thus upon the relative concentrations of reagents quite as much as upon their affinity. This then is a second aspect of the science of energetics which applies to chemical action.

Formerly the chemist measured or weighed the substances which he put together; and then measured and weighed the ultimate results, wrote an equation and heaved a sigh of satisfaction at having mastered the mechanism of the reaction. Since the ideas above related have been introduced, we strive to follow the reaction while it is going on, to detect the molecules at work. We must often devise special methods for such a purpose and many difficulties have hitherto seemed unsurmountable. But when we do obtain such glimpses, we become more and more convinced of the fewness and simplicity of the fundamental ideas which we require for a basis of the science.

In any simple reaction, there is a perceptible interval of time between the mixture of the ingredients and the completion of the ultimate result. Why is this? Because a measurable interval elapses before all the molecular changes have taken place. This will depend, as pointed out above, first upon the readiness with which the exchange takes place (a question of affinity), secondly upon the frequency of meeting of the reacting molecules. Molecules will meet more freely if there are more of them in a given space, and if they move faster through added energy; and colliding molecules of

the two reacting substances will combine more frequently, the greater their mutual affinities. This relation of chemical change to time is one of the most important aspects of modern physical chemistry.<sup>1</sup>

In recent years it has become possible to produce an intense cold, and it has been observed in the laboratories of Professor Dewar and others, that as the temperature decreases, the speed of reaction also decreases. Furthermore, it has long been known that matter usually contracts, that is to say, occupies less space, as it grows colder. At a temperature minus 273° centigrade, all heat energy ceases, all chemical reactions become exceedingly slow, and all volume approaches as near as possible to nothing without the actual disappearance of substance. It is fair to assume that at such an absolute zero various other properties by means of which we differentiate substances would disappear, and this, too, is verified by recent observations. Nevertheless, all substances by no means become identical at this point. Because heat is a form of energy, and cold is only the absence of that form of energy, we have here only another aspect of the ever-recurring effect of the changing relation of matter to energy in producing the phenomena of our actual world.

In summing up the outcome of our work in this lecture, it is clear that we have built a sort of platform, floating upon a sea of uncertainty, but of sufficient strength and stability to permit the erection of a more solid edifice of physico-chemical theory. Let us cast another glance at the planks. We have the four fundamental ideas, matter, energy, space and time — which occur in everything superposed upon one another but not in a constant quantitative ratio; these abstract es-

<sup>1</sup> An experiment demonstrating the effect of concentration and temperature upon the speed of reaction is given at the end of the Appendix to this volume. [Editor.]

sences coöperate in the manifestation of chemical *substances*, of kinetic energy of motion, and of potential energy of position. I think that you will agree with me that although we may not be generally aware of it, these four fundamental conceptions work together in our minds and our senses in producing all our perceptions of the chemical phenomena of nature.

## OSMOTIC PRESSURE AND THE DETERMINATION OF MOLECULAR WEIGHTS<sup>1</sup>

WITHIN recent years it has become more and more apparent that an intimate connection exists between the stoichiometrical composition of a solution and its physical behavior. While earlier efforts towards proving this assumption were unsuccessful, chiefly because the experimental material was almost wholly confined to aqueous solutions of salts, which offer peculiar obstacles to such an investigation, F. Raoult's<sup>2</sup> patient researches upon organic substances in more varied solutions have enabled him to formulate accurately the long-expected laws, and to put the chemical world under lasting obligation for new methods for determining molecular weights under very favorable conditions. Raoult's law would read, in its most general form: In dilute solutions the depressions of the vapor tension and of the freezing-point of the solvent vary directly with the ratio between the numbers of molecules of solvent and of substance dissolved in the mixture. Provided there be no chemical action involved in the process of solution, this relation is entirely independent of the nature of the substances.

Within the ordinary range of conditions, the *freezing-point* of a pure liquid is constant; according to Raoult's law, every molecule of foreign matter occasions the same constant depression. Every liquid, however, has its own constant coefficient of depression, which may be found by determining the depression caused by the presence of one molecule of any substance in one hundred molecules of the liquid.

<sup>1</sup> A brief review of preceding work published in the *American Chemical Journal*, **12**, 130 (1890).

<sup>2</sup> *Compt. rend.* **87**, 167 (1878); **95**, 1030 (1882).

The *vapor tension* of a liquid is not constant within the range of ordinary experimentation, since it is a complex function of the temperature and of the nature of the substance. But Raoult has shown that its depression shows a relation to percentage of foreign molecules which is independent of temperature, provided he expresses the depression, not in absolute measure, but as a fraction of the tension of the pure solvent at the same temperature. Then the molecular depression, i.e., the product of the molecular weight of the substance dissolved into the relative depression of a one per cent solution, becomes a definite constant for any substances which that particular liquid may dissolve. It is noticeable that this constant's numerical value always approaches very nearly  $\frac{1}{100}$  of the molecular weight of the solvent. The constant is therefore likewise independent of the nature of the solvent; one may generalize for *all* solutions, that the tension of the pure solvent is to the actual depression as is the number of molecules of solvent to the number of molecules of substance dissolved.

Laws as simple as these point to conditions, in solutions, very like those existing in the gaseous state. How great this analogy is has been shown in the well-matured papers of J. H. van 't Hoff<sup>1</sup> on osmotic pressure. Osmotic pressure is the name given by van 't Hoff to the force with which a liquid will enter into a cell containing the solution of some substance in that liquid through walls which are pervious to the solvent alone. Pfeffer<sup>2</sup> has shown that when such a cell is put into a vessel containing the pure solvent, the latter will enter the cell, increasing the bulk of the solution within, until this tendency is counterbalanced by the difference of level in the two vessels or some other pressure. The pressure

<sup>1</sup> *Z. physik. Chem.* **1**, 481 (1887).

<sup>2</sup> Monograph, *Osmotische Untersuchungen*. Leipzig, 1877.

required to counterbalance this tendency toward endosmose is always the same for the same concentration of the solution, and for different concentrations is found to be proportionate to the number of molecules dissolved in the unit volume. Whether this osmotic pressure be due to the motions of the dissolved molecules or to the attraction of some other sort which they exert upon the solvent, it is evident that the effect must depend upon the number of molecules per unit volume only when the molecules of the dissolved body are free to act independently of each other, as do the molecules of a gas. What the real kinetic energy of the molecules in such a solution is, we do not decide by drawing this conclusion. Even if it be as great as in a gas, the great resistance which a solvent opposes to diffusion shows that there is a force which greatly diminishes the external effect of this kinetic energy; it can never, therefore, have occurred to van 't Hoff to claim that osmotic pressure is to be measured externally in the same absolute unit as gaseous pressure. But this opinion seems to have gained a foothold, so that the kinetic treatment of the subject is combated by M. Pupin,<sup>1</sup> on the ground that the kinetic energy of the molecules in a solution ought to burst the containing vessel when it was concentrated to what would correspond, in the gaseous state, to a volume under the pressure of many atmospheres. For this reason he demands that osmotic pressure should be treated as a *static* phenomenon. To the writer, Dr. Pupin appears to confound *molar* and *molecular* kinetics. Because the mass as a whole is in equilibrium and at rest, it does not follow that the molecules must be; in fact very few physicists would care to call any force *static* in the sense that it was not occasioned by kinetic forces held in equilibrium for the moment.

<sup>1</sup> Dissertation, *Der osmotische Druck*, etc., University of Berlin, 1889.

That the vessel is not exploded by the pressure of the molecules, as Dr. Pupin demands, is due to the same force of solution which prevents their evaporating at the free surface. How great this force can become we may guess from the enormous condensation taking place in the absorption of gases by liquids; that the force is a *kinetic* one is shown by its being a function of temperature, a purely kinetic phenomenon. Bredig<sup>1</sup> has recently endeavored to show how this force can be made to diminish the external effect of the kinetic energy of the molecules of dissolved substance in such a manner that there is still freedom of action within the mass; and upon this line of reasoning we must depend for a final explanation of the phenomena.

For van 't Hoff it was, however, sufficient that an osmotic pressure does exist which is dependent upon the kinetic energy of the molecules. By simple application of the method of Carnot's cycle, he shows that the osmotic pressure must be proportional to the absolute temperature, and that, for solutions of gases, it corresponds precisely to the tension of the gas in the solution. A natural inference from all this is that Boyle's, Gay-Lussac's, Henry's, and Avogadro's laws find their counterparts in the laws governing osmotic pressure.

Suppose now solutions of two different substances in the same solvent to possess the same tension for the vapor of the latter; it is necessary that they shall also have the same osmotic pressure. For suppose them separated by a wall which is permeable to the solvent alone, but with their free surfaces in communication through the atmosphere. The vapor tension of both being the same, a little of the solvent might distill from one solution to the other without the performance of any work; but if at the same time their osmotic

<sup>1</sup> *Z. physik. Chem.* 4, 444 (1889).

pressure were different, work *would* be performed by the re-transfer of the same quantity of solvent through the membranous wall; this would mean a continuous process in an isolated system, attended by gain or loss of energy. As this is impossible, equal vapor tension means equal osmotic pressure, and vice versa. Consequently the same number of molecules always produce the same depression of vapor tension in a solvent. Exactly the same sort of reasoning would show that solutions having the same freezing-point have like osmotic pressures. Both of these laws are identical with those found empirically by Raoult. Thermodynamic reasoning further shows that the molecular depression of vapor tension is indeed one hundredth of the molecular weight of the solvent, while the depression of the freezing-point depends more directly upon the nature of the solvent, being

$$\text{a function of its latent heat of liquefaction: } t = 0.02 \frac{T^2}{W}, \text{ where}$$

$T$  is the absolute temperature of congelation of the pure solvent,  $W$  is the latent heat per kilogram, and  $t$  is the molecular depression.

These are the main results of van 't Hoff's deductions, as far as molecular weight determinations are concerned. They enable us to employ for this purpose, with perfect confidence, observations upon the phenomena of evaporation, freezing, and osmose.

The direct measurement of osmotic pressure, as was done by Pfeffer, is difficult and not universally feasible. On the other hand, de Vries has shown how to compare such pressures by means of plant cells.<sup>1</sup> It is found that the living pro-

<sup>1</sup> Pringsheim's *Jahrbücher für Wissenschaften. Botanik*, **14**, 4. See also *Z. physik. Chem.* **2**, 414 (1888). Donders and Hamburger have shown that the same phenomena can be studied in the behavior of blood-corpuscles; *Archiv. für Anatomie und Physiologie, Physiolog. Abth.* 1886, 476, also Hamburger, *Maanbl. Nat. Wetensch.* 1889, 63.

toplasm of such cells, placed in a solution whose solvent only can penetrate the membrane, will yield water to the solution if the latter be concentrated, while it will take it up again if the solution be diluted. The protoplasm will therefore recede from the walls of its cell, or again approach it, and this expansion or contraction can be observed with the microscope. By systematic dilution, a point may be determined for every substance where it is isotonic with another, i.e., will neither expand nor contract a protoplasm which had come to rest in the other. Interesting as this method is, and capable of yielding good results in the hands of a skillful microscopist, it is hardly useful in the chemical laboratory, where, aside from lack of familiarity with microscopic work, the investigator would be hampered by the exclusion of all substances which will kill plant life.

The freezing-point method has recently been reviewed in this magazine; it therefore only remains for the writer to express his view of its scope. While originally only those few liquids were used as solvents whose freezing-points approached that of water, recent investigators have successfully employed substances like paraffine and the more fusible metals as the solvent; there are, therefore, few substances which are not amenable to the method. But the following errors should be avoided: the use of thermometers not sufficiently sensitive to admit of observations at high dilutions; contenting one's self with observations within too limited a range of concentration to exclude a chance of overlooking abnormal behavior at some point; allowing too great a change of concentration to occur through the separation of the solvent in the solid state; using solvents which have a chemical effect upon the substance under investigation. Substances dissociate in one liquid which remain in complexer molecules in another. Chemists, in applying Raoult's methods, must remember

that all electrolytes behave abnormally in aqueous solutions, and that the presence of hydrates may affect the result.

The method of determining the molecular weight from the vapor tension of the solution is not yet applied so generally; but its scope is even greater, because the range of solvents and of temperatures is so largely increased. Raoult and Planck<sup>1</sup> have shown independently of each other that the formula for the molecular weight of the dissolved substance is

$$M = M_0 \frac{p f'}{f - f'},$$

where  $M_0$  is the molecular weight of the solvent,  $p$  the percentage of substance in 100 grams of solvent,  $f$  and  $f'$  the tensions of the pure solvent and the solution respectively.

Raoult measures  $f$  and  $f'$  by the heights of the mercury in eudiometers containing the liquids. A knowledge of the true value of  $p$  depends upon the determination of  $f'$ , as part of the solvent leaves the solution as vapor under that tension; therefore an error in determining  $f'$  affects the result three times in the same direction. The method is less exact and more inconvenient than that of determining the freezing-point.

A dynamic way, applied under Ostwald's direction by Walker,<sup>2</sup> is very much easier: determine the amount of water which different solutions will yield to the same amount of air. The measurements are made on the balance, and the apparatus consists of one set of bulbs to contain the solution, another to hold an absorbent for water, and an aspirator. The method has been generalized by Will and Bredig<sup>3</sup> for other solvents.

Lowering the tension means raising the point of ebullition

<sup>1</sup> *Z. physik. Chem.* **2**, 353 seq., 405 seq. (1888).

<sup>2</sup> *Z. physik. Chem.* **2**, 602 (1888).

<sup>3</sup> *Berichte*, **21**, 1084 (1889).

for normal pressure, and the boiling-point is, of course, capable of most exact determination. The method has been elaborated by Beckmann,<sup>1</sup> while the reader will remember a recent paper by Wiley on this subject, which does not, however, give sufficient details, as Beckmann's paper had already been announced.

The latter's apparatus consists of a vessel of about 100 cc. capacity, having a rounded bottom and three necks. Of these, the central one connects with a Soxhlet condenser, the second carries a Beckmann thermometer, whose bulb is completely submerged, and the third neck serves for the introduction of the substance.

Steady boiling is assured by filling the vessel to a certain height with beads or garnets, and by sealing platinum wires into the bottom to promote conduction. The pure solvent is first raised to the boiling-point, its temperature noted, and the weighed substance is thereupon introduced. As soon as the thermometer has become constant, the rise is noted; a fresh quantity of substance may then be introduced, and the observation repeated. The formula for the molecular elevation of the boiling-point is precisely like that found by van 't Hoff for the freezing-point,

$$t = \frac{0.02 T^2}{W},$$

with the exception that here  $T$  means the boiling-point of the pure liquid and  $W$  its heat of vaporization. The constant  $t$  being found by calculation or experiment, whenever we determine that for  $p$  grams of substance to 100 grams of solvent there is an elevation  $e$ , the molecular weight of the substance being  $M$ ,

$$M = \frac{pt}{e}$$

<sup>1</sup> *Z. physik. Chem.* **4**, 532 (1889).

, The experimental data to show the value of this method have not been published as yet, but it appears to be destined to play as great a part as does the freezing-point method introduced in its most convenient form by the same chemist.

## ELECTROLYTIC DISSOCIATION: A REVIEW OF THE HYPOTHESIS OF SVANTE ARRHENIUS<sup>1</sup>

IN 1857, almost simultaneously, Williamson and Clausius put forward the hypothesis that, in the fluid state at least, the molecules of compounds are not stable, in the sense that they are persisting aggregations of the identical molecules which originally united to form them; on the contrary, it was assumed that these molecules in so far resemble living organisms that, while the external appearance remains unchanged, the constituents are constantly being cast off and replaced by new ones of the same kind, so that there must always be a few molecules in a state of *dissociation*. This hypothesis has been favorably regarded as an explanation of the possibility of the coexistence of two opposing reactions, like those of etherification and saponification, where it is left to the chance encounter of molecules to occasion the existence of water and ether, or of alcohol and acid; it has likewise been regarded as a plausible explanation of the readiness with which an electrolyte will obey the influence of currents so feeble that their energy should not suffice to decompose a single molecule whose atoms were held together by their full chemical attraction. But when, six years ago, the attempt was made by Arrhenius to give a quantitative expression to the hypothesis and to apply it to the explanation of all the anomalies observed in the physical behavior of solutions, much latent hostility was called forth, and a general discussion was aroused, which has continued until the present time. It appears, however, to the reviewer that a point has now been reached where the burden of proof should rest upon the opponents

<sup>1</sup> Reprinted from *Am. Chem. Journ.* **12**, 506 (1890).

rather than upon the supporters of the hypothesis. An analysis of this discussion, set forth in proper order, might prove both lengthy and confusing, and I therefore relegate a chronological list of the original papers to the end of this review and confine myself to a brief exposition of the hypothesis as it stands at present, and of the chief objections which have been raised to it.

The fundamental idea is this: In electrical conductors of the second class electricity can be *transported* only by electrically "active" molecules, i.e., those in which the electrostatic charges are not neutralized within the molecule; the *ions* are able to receive and transport charges, positive and negative respectively, as long as they are separated, but not when they are firmly knit into a neutral molecule. It follows that there can be no conduction without a preëxistent partial dissociation of the molecules, which may be occasioned either by heat or more generally by the presence of a foreign body, such as water. It is, for instance, a well-known fact that some of the best conductors, like the strong acids, become insulators when freed from the last traces of water, while water itself is classed among the poorest conductors when free from impurities. The mechanism by which water, *par excellence*, should produce electrolytic dissociation, while alcohol and other solvents do not, has yet to be explained; it does seem strange that such an effect should be produced without a corresponding dissociation of the water, an idea which Arrhenius rejects or admits only to a minimal extent. However that may be, electrolytic dissociation is assumed to be a phenomenon closely corresponding to gaseous dissociation and obedient to laws expressed by the same thermodynamic formulæ, with this difference, that "osmotic" pressure must replace gas pressure. Consequently, dissociation must be increased by dilution (increase of volume) and by heat; but

for different substances the corresponding coefficients may differ.

1. The first application of this hypothesis affects Kohlrausch's law of conduction;<sup>1</sup> the conducting power of an electrolyte is no longer the sum of the velocities of all the ions, but of that proportion which are free to move. Only for extreme dilutions do we find a rigorous adherence to the equation  $\lambda = u + v$ , which becomes in less dilute solutions  $\lambda = \alpha(u+v)$  (I), where  $\alpha$  expresses the "coefficient of activity," or that proportion of the whole number of molecules which is dissociated. Experiments having given very reliable results for  $u$  and  $v$  in the case of quite a number of ions, and  $\lambda$  being known for a large number of compounds at various degrees of concentration, the respective values of  $\alpha$  are readily obtained.

2. The number of molecules in the solution is increased by the dissociation. If each molecule is dissociated into  $k$  constituent ions, and  $n_1$  molecules are thus broken up, while  $n$  remain associated, the osmotic pressure must correspond to the presence of  $n+kn_1$  molecules, instead of  $n+n_1$ . We shall have for the relation of the true osmotic pressure to that calculated upon the assumption that the molecules remain intact,  $i = \frac{n+kn_1}{n+n_1}$

The definition of the coefficient of activity has introduced the value  $\alpha = \frac{n_1}{n+n_1}$ , whence

$$i = 1 + (k-1)\alpha \quad (\text{II})$$

This explains the fact, alluded to in a recent review, that the molecular weight of an electrolyte, as determined by any of the "osmotic" methods, must be found smaller than

<sup>1</sup> Compare *Am. Chem. Journ.* 11, 116 (1889).

theory would require. The coefficient  $i$  has been determined for many electrolytes, both by the freezing-point method and de Vries's and Hamburger's isotonism methods, and has in almost every case been found to agree astonishingly well with the corresponding value obtained from equation II, after calculating  $a$  by equation I. The few exceptions are found for salts which behave anomalously in other respects, and can be explained by making further assumptions which need not be discussed here.

3. If  $k=2$ , that is if the electrolyte consists of but two ions, as in the case of monobasic acids and their salts with monovalent metals, the dissociation ought to obey the law which has been found to hold for gaseous dissociation where one molecule breaks up into two constituents,  $\frac{p_2}{p_1^2} = \text{const.}$ ,

$p$  now referring to the *osmotic* pressure of the integral molecules and  $p_1$  to that of either set of ions of the dissociated ones. The osmotic pressure depends upon the number of molecules in the unit volume of solution. Therefore, if we call the volume of the solution  $V$ ,  $p = \frac{n}{V}$ ,  $p_1 = \frac{n_1}{V}$ , and  $\frac{nV}{n_1^2} = \text{const.}$

If the dissociation were complete, a result reached at infinite dilution, the molecular conductivity would reach a maximum value  $\mu_\infty$ , but at the finite dilution  $V$ , it has a smaller value  $\mu_v$ , which is a measure of the number of dissociated molecules in the total. We can substitute in the last equation the value  $n_1 = \frac{\mu_v}{\mu_\infty}$ , and  $n = 1 - \frac{\mu_v}{\mu_\infty}$ , and obtain

$$\frac{\mu_\infty (\mu_\infty - \mu_v) V}{\mu_v^2} = C$$

In this form the ratio has been examined by Ostwald, and has been found to remain practically constant for any

one substance from one-fourth normal solution up to the very highest dilution amenable to experiment. For different acids, this constant assumes different values which have proved to be closely connected with the chemical activity of

these acids. Putting  $m = \frac{\mu_\infty}{\mu_v}$  and  $K = \frac{1}{C}$ , we can note for refer-

ence the equation to which Ostwald now reduces his results:

$$\frac{m^2}{(1-m)V} = K \quad (\text{III})$$

4. If the solution of an electrolyte really contains free ions, how is it that this does not at once become apparent, either by the decomposition of water, or by some physical heterogeneity of the system? The answer lies in the further definition that these free ions bear equal and opposite electrostatic charges, which do not permit any local preponderance of one sort of ions over another, as this would mean a local accumulation of electricity in a system which is in equilibrium. Consequently — although the ions travel with different velocities — if they are traveling in the same direction as in diffusion, the attraction of their electrostatic charges compels them to accommodate their rates one to another, so that the slower ion is accelerated while the faster is retarded; the rate of diffusion of the salt is therefore intermediate between the velocities of the two ions. These conditions have received a rigorous mathematical formulation, and the close agreement between the theoretical and experimental results affords a beautiful confirmation of the fundamental hypothesis. (Nernst.)

5. Any cause, on the other hand, which produces a relative dislocation of the positive and negative ions must occasion electrical heterogeneity, showing itself by differences of potential at different points. Upon this idea a plausible

"osmotic" theory of voltaic electricity has been based and substantiated by experiment. (Nernst.)

6. Conversely, any difference of electrical potential in the solution must produce a motion of the ions. Here we have the Clausius hypothesis of electrolysis. The introduction of electrodes disturbs the equilibrium of the solution, the positive ion moves to the cathode, where it gives up its charge, while the negative ion does the same at the cathode. It is only when the ions are relieved of their charges that they are capable of attacking the metal of the electrodes, or of decomposing water, causing the well-known secondary effects; charged, and in the paralyzing presence of an opposite charge, they are supposed to be incapable of doing this. In this connection may be cited an experiment which appears incomprehensible unless free ions are assumed to exist in the solution. Dilute sulphuric acid, contained in a flask whose exterior was coated with tin foil, was connected by a wick with a Lippmann electrometer; upon giving a positive charge to the exterior of the flask the electrometer indicated the presence of positive electricity, and some bubbles of hydrogen were evolved near it. Consequently, the flask, being a modified Leyden jar, negative ions ( $\text{SO}_4^-$ ) had collected on the interior, while the corresponding hydrogen had been driven over toward the electrometer.

7. Properties like density, refractive power, capillarity and viscosity of saline solutions, whose numerical values appear to depend upon the sum of two factors characteristic of the acid and of the metal, should show this additive nature best where the salts are most dissociated; this appears to be the case.

8. We have now to consider the chemical side of the hypothesis, and we are met by the startling assertion that those acids show the greatest degree of dissociation which we

consider the strongest. Indeed, according to Arrhenius, chemical activity depends upon the degree of electrolytic dissociation, only the dissociated molecules being capable of entering into reaction. A fundamental difference is hereby inferred to exist between reactions among electrolytes and reactions introducing only non-electrolytes, or, to recall antiquated notions, between reactions which involve substances of the water and hydrochloric acid types, and those involving merely the hydrogen and ammonia types. Valid objections raised to this distinction would upset the theory from the chemist's standpoint: examples in favor of the distinction have been adduced, such as the fact that the characteristic halogen reaction with silver nitrate is only shown by such compounds in which the halogen can be supposed to exist as a free ion, while with those which contain the halogen within the radicle, like trichloracetic acid, the reaction fails. Considering by themselves the reactions between electrolytes, it is noticeable that the presence of water or another solvent appears to be necessary (cf. the passivity of absolutely dry gases). The law of Guldberg and Waage must be modified in so far that the speed of reaction is not a function of the total masses of the electrolytes in solution, but of the masses of dissociated ions: van 't Hoff has introduced the coefficient  $i$  (isotonic coefficient) successfully enough into these considerations, and  $i$  has already been shown to be a function of  $\alpha$  (II). In the acceleration or retardation of etherification and saponification, the acids and bases must act proportionately to their stages of dissociation, so that Ostwald's old affinity-coefficients must correspond with the values of  $k$  in equation III, which is also found to be true; for the same reason the effectiveness of weaker acids (non-dissociated) increases more rapidly for additional dilution than does that of stronger acids which are much nearer their

limit. The evidence to be obtained from the study of the kinetics of chemical reaction all appears to favor the theory.

9. New ideas are introduced with regard to chemical equilibrium. The laws of dissociation, where gases are concerned, lead to the well-established postulate that dissociation shall be greatest where the atmosphere contains no excess of either of the constituents into which the molecule will break up; dissociation is unaffected by the presence of any other *indifferent* substances. By analogy, if a solution already contains a number of free ions of a particular sort, any substance consisting in part of this same sort of ions will not dissociate as fully as in pure water. Consequently an acid will be weakened by the presence of one of its neutral salts, but the effect will be much more perceptible for a weak acid than for a strong one. This has been verified by Arrhenius. Comparing on the other hand, acids which have the positive ion  $H$  in common, a mixture of the two must affect their respective degrees of dissociation, unless before mixing the  $H$  had the same osmotic partial pressure in both solutions. This means that there shall be the same degree of dissociation in the two solutions, that they shall be "isohydric." Under such conditions, if  $m$  parts of one solution having the conductivity  $a$  be mixed with  $n$  parts of the other having the conductivity  $b$ , the resulting solution will conduct as if each electrolyte were conducting independently and unchanged. Its conductivity is  $\frac{ma+nb}{m+n}$ , no matter what the relative values of  $m$  and  $n$  are. Furthermore, if two solutions are "isohydric" with a third, they must be isohydrous with each other. These two consequences have been substantiated by the examination of the conductivity of mixtures of "isohydric" solutions of acids with one another and with those of their respective neutral salts, of neutral salts with one another and with the

solutions of their respective bases, and finally of the bases with one another.

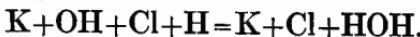
But if solutions are mixed together which are not "isohydric," the resultant conductivity will be greater than  $\frac{ma+nb}{m+n}$ , if calculation shows that the stronger acid is thereby

partially reassociated and the weaker partially dissociated, while it will be less than the normal if the stronger acid is being dissociated and the weaker reassociated. This depends upon the fact that the dissociation of the same number of molecules produces a relatively greater effect when the acid is farther from the limit of dissociation which all approach asymptotically. In keeping with these facts is Nernst's observation that the solubility of a salt is decreased by the presence of compounds having a common ion with it; thus the solubility of silver acetate is equally affected by the presence of silver nitrate and sodium acetate.

10. The theory of "isohydric" solutions leads up to the important point of the neutralization of acids by bases. In the first place, salts in dilute solutions are no longer considered to be the product of a reaction like the following:—



Where there is perfect dissociation, at extreme dilutions, the reaction is represented thus:—



At greater concentrations this is accompanied by a certain reassociation of  $\text{K} + \text{Cl}$  and a dissociation  $\text{K}$ ,  $\text{OH}$  and  $\text{H}$ ,  $\text{Cl}$ , but  $\text{K} + \text{Cl}$  is supposed to be very small in all cases, as the dissociation of salts proves to be relatively very great. Neutralization would therefore practically mean a formation of water from  $\text{H}$  and  $\text{OH}$ , and salts as such would only exist in concentrated solutions or as a combination of a very weak acid with a very weak base. A result of this would be that

the heat of neutralization in dilute solutions should be the same for all sorts of strong acids and bases, and should, in fact, equal that produced by the reaction  $H+OH$ , a very familiar fact. Mixtures of such salts should not be accompanied by a heat effect, which explains the phenomenon of thermo-neutrality. But a weak base or a weak acid introduces the positive or negative heat of dissociation pertaining to it; consequently the thermal effect of neutralization must vary from that of  $H+OH$ , but this variation must decrease with the increase of temperature. If a stronger and a weaker acid are together mixed with a base, it is only the *weaker* anion which really *unites* with the metal to a limited extent, while the stronger anion keeps the relatively greater amount of metal in electrolytic dissociation, *their* neutralization being characterized by the union of their former conjugates  $H+OH$ . It is noticeable that electrolytic dissociation is to be sharply separated from the *hydrolysis* of sugars and of very weak salts like ammonium acetate, in which the reaction belongs rather to the class of non-electrolytes, although electrolytes are involved.

A final point with regard to chemical equilibrium is this, that when equilibrium has been reached in a solution containing a number of electrolytes, each one of these is in a state of dissociation, which depends upon the equilibrium of osmotic pressure between the non-dissociated molecules and all the free ions of the kinds which compose it. A distribution of metals and acids as it is usually assumed in older views is therefore rendered out of question, because a *free* ion belongs neither to one compound nor to another, it merely counterbalances that free ion of opposite charge nearest which it happens for the moment to be.

Having sketched Arrhenius' hypothesis, with some of its logical consequences, the task of judging it must be left to

those readers who will compare the mass of experimental material and will convince themselves of the simple relations which the various phenomena appear to bear toward each other. As far as this test is concerned, the hypothesis will be found to fulfill its purpose. Shall it therefore be accepted?

The objections which have been raised are twofold, physical and chemical. Oliver J. Lodge concedes the ingenuity and physical "orthodoxy" of the treatment, and it might appear that his criticisms to the earlier papers have been largely obviated by the further development of the theory; indeed they apply chiefly to points which I have omitted as no longer seeming essential to the theory, such as relations between the viscosity and the friction which a solvent opposes to the motion of the ions. But he appears mainly to object to the neglect of conduction by the solvent, which he believes would explain the rate of transference of the ions, without the assumption of unequal velocities of negative and positive ions. It is doubtful whether such an explanation would also elucidate the troublesome diffusion phenomena as well as does "dissociation" in the hands of Nernst. E. Wiedemann thinks that hydrates are the cause of better conduction, and explains osmotic anomalies by the assumption of a polymerization of the solvent. Aside from Planck's proof, on thermodynamic grounds, that such polymerization would not affect the vapor tension phenomenon in this way, in very dilute solutions, Ostwald pertinently asks why the electrolyte need cause a polymerization which no non-electrolyte does.

The objections from a chemical standpoint have been chiefly raised by Henry E. Armstrong, and are not all cogent. The following appear to be the most important at the present time:—

1. Anhydrous hydrochloric acid and pure water do not

conduct, while fused silver iodide does, which is an anomaly. Arrhenius finds an explanation in the dissociation of silver iodide by heat.

2. Hydrochloric, hydrobromic and hydriodic acids differ markedly in stability, but they are all assigned the same dissociation ratio. This is evidently a case of misapprehension, as the instability lies in the negative ion itself, and not in the compound.

3. Why does not alcohol dissociate electrolytes as well as water, and why does not water conduct?

4. According to Ostwald's measurements, phenylpropionic, cinnamic, and phenylpropiolic acids range in the order of their conducting power, —



Therefore that acid is *most* dissociated which can *least* spare its hydrogen.

This argument illustrates the necessity of keeping the types of reactions apart. Nothing appears to justify his assumption that the carboxyl group should be affected in this way by what happens in a neighboring group, where hydrogen plays an entirely different rôle.

The main opposition to the dissociation hypothesis is to be found in a rival hypothesis which has found advocates in Mendeléeff, Armstrong, Pickering, Crompton, Bonty and E. Wiedemann,—the “hydration” hypothesis connected with the “residual affinity” idea. Bonty holds that electrolytes are of two classes, those in which both ions show equal rates of transference, and the “abnormal” ones, in which this is not the case. All abnormal salts are said to be capable of forming hydrates and do so. The law of equivalent ratio holds absolutely in so few cases that these considerations may be dismissed, in view of the more powerful ideas of Kohlrausch. E. Wiedemann argues from the change of color of

salts of nickel, copper, cobalt, etc., upon dilution and heating, effects which Arrhenius ascribes to a difference in color between the free ion and the compound. Armstrong and Pickering present the "residual affinity" theory with much vigor. The atomic valences are not assumed to be whole numbers, so that it rarely happens that the positive and negative valences in a compound just balance. Consequently, a small residual affinity remains to each molecule, by virtue of which larger aggregations are formed, molecular compounds, either among the molecules of the same sort or with the molecules of the solvent. Armstrong's valences represent the old Berzelian negative and positive electricities, which cause their respective atoms to tend to opposite electrodes during the passage of the current, the atoms being set free by the complexes "straining" at each other as they pass each other. The idea of unequal electrical charges appears incompatible with Faraday's law that the current produces the same effect in all electrolytes. Pickering bases his opposition upon more modern ideas, separating affinity from electric charges, and sees in the phenomena of electrolysis and dilution effects of the dissociation and formation of various hydrates. The basis for this lies in the observations by Mendeléeff, Pickering, and Crompton, that various properties of acids and salts, such as conductivity, density, the heat of solution, when plotted as ordinates, with the percentage composition of the solution as abscissas, do not present regular curves. A study of their first or second differentials would appear to reveal the presence of points of abrupt change, and these points are supposed to represent definite chemical compounds. It does not appear that Arrhenius has entirely invalidated the proofs of the existence of such compounds, and there is no doubt that they present a very awkward obstacle to his theory, which he has still to sur-

mount. On the other hand, Pickering's explanations of the phenomena of freezing are extremely complex, and I am not aware of any positive attempt to explain facts like diffusion upon them. The thermo-chemical phenomena might be fairly explained by Pickering's reasoning.

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## A BRIEF REVIEW OF WILHELM OSTWALD'S "GRUNDRISS DER ALLGEMEINEN CHEMIE" <sup>1</sup>

A SINCERE admirer of Professor Ostwald's monumental "Lehrbuch" must regret that the present textbook should have been chosen to present the recent developments of physical chemistry, rather than a second edition of the earlier, larger work. While the present volume is intended, according to the preface, to interest in physical chemistry those as yet unacquainted with the subject, it seems questionable whether this object can best be obtained by cutting away much that renders the larger work such delightful reading; nor does it seem plausible that a non-mathematical mind should grasp a mathematical formula better because the strict proof is omitted as too abstruse, and that the reader who is conversant with calculus should therefore be debarred from this aid to the comprehension. There is no doubt, however, that this little volume gives all the subject-matter proper of the two older volumes, with some additions; condensation has been obtained by employing smaller type, omitting many tables and much purely historical matter, and, finally, by omitting all references to titles of papers, instead of which the year of publication has been inserted in the text. The chapters have been rearranged into a very logical sequence, and the new points of view introduced by the hypothesis of osmotic pressure receive a very full and withal very comprehensible treatment.

For such as desire a rather hurried glance over a large field, this book can be very well recommended; but it is to be hoped that its presence in the chemist's library will not be supposed to atone for the absence of the "Lehrbuch."

<sup>1</sup> Reprinted from *Am. Chem. Journ.* **12**, 516 (1890).

## THE PROVINCE OF A GREAT ENDOWMENT FOR RESEARCH<sup>1</sup>

IN response to the request for the views of American men of science on the mission of the Carnegie Institution, I would first of all express the hope that the trustees will reject those propositions which would most seriously menace the free development and untrammeled activity of our various scientific bodies and institutions of learning — especially the establishment of a huge reserve fund, with the annual distribution of its income among the "deserving poor." It seems to me that, while there may be occasional demands for large sums to equip exploring parties on behalf of some of the descriptive sciences, the legitimate demands for assistance in research in the exact sciences ought not to be very large, in any one year; in fact, I venture the assertion that the existence of large sums to be devoted in this way might lead to wastefulness in methods, rather than to the development of that resourcefulness which has been the characteristic of the greatest investigators. Favored beneficiaries might choose a field of work from which others would be debarred by questions of cost, rather than strike out upon lines of greater originality and importance. Again, it cannot be denied that the establishment of a standard of measurement with the utmost precision is work well worthy of national support: but if the Carnegie Institution were to encourage, by means of its stipends, all our most capable physicists to devote themselves to this class of work, advance in this department of knowledge would be seriously hampered. Is it a hardy prediction, however, that the votes of

<sup>1</sup> Reprinted from *Science*, N. S., vol. 16, 1902, pp. 485-86.

a committee on distribution would always favor such definite projects, as against a proposition to explore some vaguely defined problem of physics or chemistry?

I think, therefore, that the proportion of the income to be devoted to the immediate subvention of research ought to be small at best; the aid would probably be more efficient, if administered through existing scientific societies, who would receive from time to time such additions to their research funds as would seem commensurate with their previous success in promoting investigation. The existence of a central reviewing body would act as a wholesome restraint upon these smaller scientific bodies, while the relative needs of investigators could be better judged by a jury of experts in their immediate field of work, than by such a heterogeneous committee as would be furnished by the trustees themselves.

On the other hand, the suggestion that the institution should play the part of a private benefactor to our universities, by adding to their endowment, building and equipping laboratories, augmenting professors' salaries or providing them with private assistants, seems to me to savor of paternalism and to open the way to serious abuses, while at the same time it might cause colleges to shape their course with the sole view of pleasing the guardians of the fund, for the time being.

It seems doubtful whether any salary could be paid to a body of academicians, sufficient to enable them to devote their whole time to research; and it is a fair question whether it would really be desirable to set a body of men apart in a scientific academy, at the present day, without that contact with students which a university provides. It must be remembered that the Royal Institution of London is not an academy in the strictest sense; nor do the resident lecturers owe a duty to a foundation, but rather to the subscribers. With the enormous distances separating our educational centres, it

would not be conceivable that a lecturer could assemble around him so national an audience as would listen to a Faraday or a Rayleigh.

All these plans remind one of the hot-house method of stimulating plant-growth; why not attempt the open-air method of cultivating the soil? The Carnegie Institution might facilitate research for all, instead of offering incentives to a chosen few. For this reason, the satisfactory equipment of marine biological stations, open to all qualified observers, and of similar institutions that would render the natural phenomena more readily accessible to general study, would seem eminently proper; while one might doubt the propriety of establishing observatories simply for the intense study of single problems. The efficacy of special research laboratories in the physical sciences, such as England owes to the generosity of Mr. Mond, has yet to be proven in contrast with that of university laboratories; to the writer, their establishment in this country would appear premature, since many of our well-equipped educational laboratories are not so crowded that they would be obliged to refuse accommodation to an independent investigator who sought their hospitality.

The same general argument would oppose the financial support of periodicals and publishing organizations, while it would strongly favor the equipment of a scientific printing office, for the prompt and cheap reproduction of the results of research, for the account of individuals as well as of associations. However, if the trustees desired to obviate the most serious difficulties which beset the American scientist in his laboratory work, they would establish workshops for the construction of special apparatus and the preparation of the more recondite materials, such as rare chemicals, microscopic mounts, etc. What stipend, for instance, could put the American chemist on a level with his German colleague, when the

latter can obtain, within twenty-four hours, any preparation that is catalogued, while the former must allow six weeks for obtaining anything that is not so commonly known as to be literally a "drug on the market"? By enabling the private investigator to supply his needs quickly and at a reasonable cost, without the unjust discrimination of "duty-free" importation, a stimulus would be given to private research, inside and outside the college laboratory. Who can estimate the amount of time frittered away in this country through the lack of ready access to the mechanical adjuncts to investigation? Workshops to supply these would not only improve our immediate condition; but, if properly organized, they might serve to educate a body of mechanicians and preparators, whose help would be invaluable in the various scientific institutions of the country.

If these suggestions should illustrate the view that the Carnegie Institution can do measurable harm by seeking to supplant private initiative with artificial stimulus, but can do immeasurable good by clearing away the obstacles that now trammel the general growth of the scientific spirit in America, they will best express the opinion of

MORRIS LOEB.

## ATOMS AND MOLECULES<sup>1</sup>

IT is often a question with the scientific student as to whether his investigation can lead to any real advancement of knowledge, or whether the outcome will merely add to the scraps of information that are scattered here and there in the storehouse of human intelligence. How often, when walking or bicycling in an unfamiliar country, does one turn into a lane, wondering whether it is to lead one into a new highway or end blindly, forcing the traveler to retrace his path! Fortunately, the many discoveries and inventions based on studies by previous generations made without any expectation of a practical outcome, have silenced those who scoff at anybody who looks for something that cannot at once be made into a scarf-pin or shoe-buttoner or patent medicine or the like.

Among the matters that will necessarily escape practical application longest are the infinitely great and the infinitesimally small. It is true enough that astronomy is a useful science to the navigator and to the geographical surveyor; but it would be hard to convince me that, for many generations to come, the price of iron will be affected by our knowledge that huge quantities of that metal exist in the solar atmosphere. Nevertheless, it gives us a wonderfully encouraging realization of the power of the human intellect to contemplate the steps by means of which this apparently useless bit of knowledge was secured. How grand is the thought that a Lilliputian man has been able to weigh heavenly bodies far bigger than the earth itself, and so far distant that our own distance from the sun becomes quite small by comparison!

<sup>1</sup> A popular address evidently delivered in the spring of 1906; the place and exact time are unknown. This address was illustrated by experiments. [EDITOR.]

Chemistry and physics, however, bring us to the opposite end of the scale, and we are led to the assumption of bodies that are so exceedingly small and so close together, that we cannot conceive of their dimensions any more clearly than we can conceive of our distance from the sun or from Neptune. The problem of estimating these distances must, therefore, appeal to us as similarly deprived of immediate usefulness.

There is nevertheless this difference. We are all convinced of the existence of the stars: we follow Herschel's description of their multitude with amazement, but we do not for a moment doubt the reality of his statements. The atom and the molecule are every now and then denied reality; that great thinker, Ostwald, who visited us this winter, has emphatically expressed the opinion that matter itself is non-existent and that the atom and molecule are conceptions which must sooner or later be abandoned. The permanence of the atom is assailed by the supporters of the new electron theory and is, in a measure, shaken by recent discoveries respecting radium and helium. How about the molecule? It is too small to be seen, too subtle to be handled and weighed as an individual. But we can nevertheless weigh and measure it by different means; and because results attained in various ways agree fairly well with one another, strong evidence is afforded of the reality of the molecule. It would be a very remarkable coincidence if three or four different processes gave us an identical measure for a certain thing and the thing itself did not exist. If, in traveling, we noticed a considerable number of railroads converging toward a common centre, we should expect to find something interesting and definite at that point. Similarly, I see evidence of the probable existence of the molecule in the fact that many lines of calculation converge upon the same order of magnitude.

The ancient philosophers who first thought concerning the

nature of substances as we see them around us, had many vague notions as to the causes from which the various properties of the substances might arise. One might almost say that the various Greek philosophers devised every conceivable notion as to the origin of matter which a sensible man could happen upon. Among these there were two which must claim our attention, because they throw much light upon the differing hypotheses about physical phenomena up to the present day. One notion was that every substance is made up of certain ingredients whose presence caused it to have its own particular properties, which were really the properties of the ingredients. Aristotle called these ingredients elements, and he mentioned as such elements, fire, air, earth and water, of which he considered earth as that which was cold and dry, water that which was cold and moist, fire that which was hot and dry, and air that which was hot and moist. More elements were added during the Middle Ages, so that the ancient alchemist spoke of six or seven different elements out of which all known substances were imagined to be composed. Now, since gold, silver and lead, for instance, are all composed of the same Aristotelian elements, it seemed natural that if one changed the proportion of these elements, lead, for instance, might be converted into silver or gold.

To the present time we have retained the word element, but we have given to it a somewhat altered meaning, because we have recognized that some of the substances thought by the ancient and mediæval philosophers to be simple are really compounds or mixtures; while many of the substances which they considered composite baffle the skill of the chemist when he attempts to disintegrate them. The simple metals are now all of them considered as chemical elements; and we were until very recently apt to look back with a good deal of scorn upon the alchemists who strove to change one metal into another.

But they were right from their point of view, just as we are right from ours, for with the knowledge that coal tar contains the elements carbon, hydrogen, nitrogen and oxygen, which are also contained in indigo, in quinine and in oil of bitter almonds or in vanilla, we attempt to convert the coal tar into one of these. The difference is that the alchemists failed while we succeed, and our success is largely based upon the experience obtained from the unsuccessful efforts of our predecessors.

The other notion which originated in Greece was that of the atoms, out of which all matter was supposed to be composed. Democritus of Abdera is supposed to have invented the suggestion that all matter is made up of little particles which have their own separate existence and move about freely until they happen to attach themselves to one another. This idea occupied the attention of some other Greeks and Romans, but during the Middle Ages it was entirely lost to view; and in fact, its real importance was only recognized after the already mentioned change had occurred in our views concerning the elements. Now, under the lead of John Dalton, we believe that the finest particles of which matter is composed that we are able to recognize, are little bodies which cannot be decomposed further by ordinary chemical means, and which behave very much as if they were little round pellets possessed of independent motion, and only influenced by those other little pellets that lie around them. These atoms must have very many properties of their own, and the different atoms do not necessarily have the same properties. When two atoms, therefore, are alike in their properties, we call them atoms of the same element; when the properties differ, they are atoms of different elements. Now, inasmuch as there are over seventy-five elements known to the chemist, there must be at least seventy-five different species of atoms. Whether these atoms are themselves made up of

seventy-five different sorts of substances is a question with which we cannot concern ourselves. Some chemists choose to believe that they are made up of only one sort of substance, arranged in different fashion for each kind of atom, and others have ideas that are even more difficult to grasp than this one. But inasmuch as the chemist acknowledges that he, at least, cannot go further in his subdivision than the atom, it is safe for us to stop there in our study this evening. We can never expect to see an atom, or to distinguish it by one of our senses from its neighbor. What, therefore, the real, actual properties of the atom may be, is just as hard for us to conceive, as it is to imagine how the inhabitants of some other planet would look. Nevertheless, if somebody tells us that there are inhabitants of Mars, we straightway fall to imagining that those Martians must look more or less like ourselves, or like something that we see on earth. In the same fashion we reason by analogy concerning the atoms, and readily reach conclusions concerning their general properties from the behavior of the substances which they compose. Nevertheless I would especially guard those of you who are interested in chemistry against imagining that we really know so very much about atoms, although we know a good deal about the elements after which they are named.

Let us in the first place attempt to get some experimental idea of the size of an atom. I take here a red substance (the well-known aniline dye called fuchsine) which is made up, as I happen to know, of several elements; and a very little of it gives, as you see, an intensely red coloration to a little water. If I pour this small amount of liquid into a measuring glass, and add to it one hundred times as much water, the color is still very distinct, and taking one-tenth of this and again diluting it with yet one hundred parts of water, you can still faintly perceive the red color. Now the original weight of the

coloring matter, which covered only the point of a knife, was barely one grain; dispersed over the great bulk of water which you see here, it nevertheless retained its pink coloration, which must be a proof to you how finely its substance is capable of subdivision without being decomposed. One faintly pink drop of the most dilute solution must contain at least one of the smallest particles of the red fuchsine; and each of these small particles or molecules must be made up of a number of smaller particles or atoms of four elements, one solid and black, the three others colorless gases with which you are undoubtedly familiar, and which make up the important parts of the atmosphere and of water. If these four elements had been merely mixed together, one would separate at once, as happens now when I mix a little carbon dust with air. Hence we conclude that in the red compound the carbon, oxygen, hydrogen, and nitrogen exist not as we know them, but with the atoms joined intimately together to form a new chemical compound; and it is only when we split this compound into a condition bordering on the fineness of the atoms, that we can be said to decompose it into its constituent parts. The point to which we can reduce the compound before it breaks up is called the molecule, often defined as the smallest portion of the compound which can exist and still retain the properties of that substance. In the dilution just shown, the molecules were very widely separated and were surrounded by molecules of water.

What, then, is the size of a molecule? This is one of the most interesting problems that has been put before the physicist, and it is a great triumph for science that four or five different methods have been discovered for determining this size, and that the results have been found to agree tolerably well with one another. We are accustomed to look with more awe on big things than on little ones; and so, when we are told,

of the distance between the earth and the sun, or of the greatness of the sun's diameter, we exclaim at the magnitude of the figure, while we talk unconcernedly of molecules. Is it, however, so easy to realize the exceeding smallness of the molecule?

The measurement of the magnitude of molecules can be performed in the following fashion. As a soap bubble expands with its increasing inflation its film can be greatly stretched. The thin bubble becomes more and more brilliant in color as it grows thinner; and then a moment comes when the film suddenly loses its color and becomes black. This is because a certain thickness between the front and rear wall of a film is required in order that the film shall show colors by reflection. When it has become colorless, we know that we have stretched it so that it no longer possesses this requisite thickness; it is thinner than the length of a wave of light. In order that it should be a continuous film, it must consist of at least one row of molecules; therefore, a molecule is less thick than the wave length of light is long. Immediately after the film is stretched to this extreme thinness, it breaks, which is a proof to us that there is not so very much difference between the magnitude of the wave length of light and the molecule.

Another interesting method of measuring the size of a molecule is to be derived from the behavior of gases as they rub upon one another, and while this involves much that could not be studied here, it suffices to say that the same results are obtained as by the previous method. Still other, but yet concordant results can be obtained from a study of the expansion of gases by heat, and their contraction under great pressure. From all these we reach the conclusion that the molecules have some real definite size, and likewise, that they consist of comparatively few atoms apiece.

In order that we may understand better what the rela-

tions of atoms and molecules are, I now take up some interesting experiments with substances that are elements; this is because we know that when we are dealing with a single element no change will occur which involves more than one kind of atom. I have here a jar of the substance originally known as oxygen, and the arrangement is such that I am able to pass this oxygen through various pieces of apparatus, illustrating properties of oxygen. By simply exposing the gas to a current of electricity I give to it entirely different properties, as you will see when I pass a little oxygen over this piece of paper, and then expose a strip of the same piece to the action of the electrified oxygen, or ozone, as it is called. You must not suppose that there is any electricity in this ozone which makes it different from the oxygen. I have here some ozone made by a totally different process, and it shows the same effect. The ozone can be converted back into the oxygen, as you will see when I pass it through this heated tube; it now has lost its power of affecting the impregnated paper; it has been converted back into original oxygen. In fact, all our study shows us that the sole difference between ozone and oxygen consists in the arrangement of the atoms; one molecule of oxygen must be assumed to contain two atoms, and one molecule of ozone three atoms.

If this were a single instance standing entirely by itself, the opinion might be attacked; but we have many similar cases in chemistry, although it is not always so easy to prove the matter as in the case of the oxygen. I have here two specimens of phosphorus, which to all appearances are entirely different in their nature; the one is a coherent yellow mass, the other is a red powder; and many of the properties are different likewise. This one is poisonous, that one not; this one catches fire with great ease, the other will catch fire only after considerable heating. Once I have set the two a-burning, however, the

result of their union with the oxygen of the air is precisely the same. The white, powdery oxide of phosphorus forms in each case, and if I take the same quantity of two kinds of phosphorus, I shall have, in each case, the same quantity of oxide formed. These facts prove that the two substances are identical in composition, although probably differing in the arrangement of their atoms. It fact, it is a common operation of the chemical manufacturer to convert yellow phosphorus into red, as it merely requires heating under pressure to effect the conversion.

Here is another element, sulphur, which shows the same tendency to appear under different guises representing different arrangements of the atoms. If I melt sulphur, it becomes a thin liquid; but on heating further it thickens and cannot be poured, even upon the inversion of the test-tube. Yet more heating converts it yet again to a liquid; and if I now pour it into water so as to cool it suddenly, I obtain the sulphur in a very remarkable condition, appearing in many respects like a gum; but it is still sulphur. This might be proved by drying it and setting it aside in a vessel entirely free from all other chemical agencies, when it would in time go back into the condition of the yellow sulphur. By kneading it in my hands, I am able to effect this conversion much more speedily.

These and various other cases of change happening to a simple substance, separated from other substances, force us to assume that the actual element has undergone no change, but that its atoms have rearranged themselves into new patterns. Such changes are best suited to make clear to you why we make the distinction between the molecules and the atoms. Every substance that we know of is supposed then to be made of molecules built up of one or more atoms. If the molecules are broken up, or their atoms rearranged, we ob-

tain different kinds of molecules, therefore different kinds of substance; but the atoms are not changed in the operation, and we know no method of changing them.

You may well ask, how can we get hold of molecules in order to study them? It is impossible to catch a single molecule and examine it, or even a hundred molecules; but we have every reason to believe that in gases the molecules behave more independently than they do in liquids or in solids. Hence when we wish to study molecules we begin by studying gases. Imagine a big globe filled with inconceivably small pellets that shoot to and fro in straight lines and never come to rest, and you have a notion of our conception of a vessel filled with a gas. Whenever one of these molecules hits the side of the vessel it pushes against it and tries to push it outwards; the sum total of countless impulses of this kind is supposed to constitute the pressure of a gas upon its confining walls. If I stand on a street corner on a windy day, the molecules of air strike my face, and I feel this as a direct pressure which seems to me continuous because there are so many billions of molecules striking my face in succession. The more molecules there are in a given space of gas, the more frequently they must hit the walls, and the greater becomes the pressure. The hotter the gas is, the livelier the molecules become; they travel faster; thus we explain the fact that heating increases the pressure of the gas upon its confining walls.

In the liquid or solid state, the molecules no longer travel around freely in all directions, but hang together, and occupy a limited portion of the vessel into which they are put, so that it is much harder to know what they are really doing. In the gas each molecule is supposed to be acting for itself, in the liquid or solid they must all act together.

Interesting evidence of the fact that molecules are little

independent bodies moving in a very definite way and having very definite size, is found in a well-known experiment known as osmose. Suppose that in this room there was a partition which was pierced by a number of narrow doors, and on the one side were a number of grown persons and on the other an equal number of children, and the order was given that they should distribute themselves equally over the total space. The children, moving more quickly, and having no difficulty in squeezing through the narrow doors, would soon get over to the other side, while the grown persons were still struggling to get through. The result would be that at first the actual number of people on that side of the room where the children had first been would be less than the number on the other side. Now, instead of persons, I take light and heavy molecules, the lightest molecules we know being hydrogen, and the molecules constituting the gases of the air being over fourteen times as heavy. In order to imitate the partition wall, I take this tube made of porous porcelain; the openings are so fine that we may well imagine the gas molecules having some trouble in getting through. If I fill the inside of this tube with air, and now fill this jar outside with hydrogen, the hydrogen will get in very much faster than the air can get out, and the result will be that we have a larger number of particles or molecules per cubic inch inside than there were originally; they have to find more room for these, and you see how they obtain it, by pressing this liquid out in a sort of fountain. If I reverse the experiment, I obtain the opposite effect. There is a rather ingenious practical application of this principle which is perhaps worth showing. Instead of holding water to be pressed out, this tube contains mercury; as the liquid metal is pressed down it will rise on the opposite side and make an electric contact, which causes this bell to ring. Instead of taking hydrogen I shall this time take illuminating gas, — and here

you see how soon an alarm is given. Such an arrangement might well be used where a dangerous or harmful gas is apt to appear; it was really invented for coal mines, in which there is a danger of the formation of explosive mixtures of lighter combustible gases with air.

In this way it is possible to distinguish, as you see, between lighter and heavier molecules. This method may be of value to the investigator, as we shall see. I have here a substance whose molecules are fairly large; they are ordinarily in a solid state, and they represent a substance which is neutral, as we say in chemistry,—a salt that has no effect upon vegetable colors. I throw a little of it upon these pieces of red and blue litmus paper, and you see that there is no change. Now a piece of this salt (which we call chloride of ammonium) is placed in this glass tube next to a porous partition wall; when I warm the salt it breaks up into two substances called ammonia and hydrochloric acid, which may be separated by the method of osmosis just used to ring an electric bell. The ammonia consists of molecules so light that it passes very readily through this partition wall, while the hydrochloric acid with heavier molecules passes less readily. You will be able to notice this when I pump air through both parts of the apparatus and let the two currents of air flow over these two pieces of colored paper. You see how the red paper is turning blue, and the blue paper is turning red; this is due to the fact that the hydrochloric turns blue paper red and more of it remains on the near side of the partition; the ammonia turns red paper blue, and more of it has gone through the partition. The experiment not only illustrates to you what I have shown before in a somewhat different form, but it also shows us that the big molecules of chloride of ammonia can be broken up into two sets of smaller molecules, which themselves differ from one another in size. We can even, although I am unable

to show it here, break up this hydrochloric acid and this ammonia into still smaller molecules, and beyond these still are supposed to be the atoms. Every rearrangement of atoms into molecules produces a new substance, and it is the marvelous ability of the atoms to arrange themselves into hundreds of thousands of ways that enables the organic chemist to build up out of three or four elements the many compounds which nature is building up for us daily and hourly in plants and animals.

Such then, is the idea entertained by the chemist of to-day concerning the nature of the mechanism carrying out the changes which it is his business to study. But we must remember that this idea is hypothetical — it is no more than a plausible guess. While the few master-minds of a century can grasp such theories as pure abstractions, uninfluenced by preconceived notions, the rest of us cannot free ourselves of the prejudices derived from the familiar phenomena upon which the theories are based. We are as little able to strip our imagined infinitesimal particles of Matter and Energy from the attributes of the grosser masses of our daily observation, as was the Greek to impart other than human qualities to his gods, whom he portrayed in human form. This is one of the reasons for the many more or less fantastic attempts to overturn the atomic theory as it now exists. I do not believe that the theory is perfect or ultimately correct, but a study of most of the attacks upon it leads to the conclusion that the attack is made, not upon the pure theory, but upon that particular image which has been set up to represent the theory in an iconoclast's intellectual neighborhood. Thus we sometimes find persons who imagine they are attacking the atomic theory, when they contend only against the gratuitous idea that atoms are hard, round pellets, rather than vortices of an infinitely elastic fluid or the like. But we have no time

to-night for these objections and criticisms, — it is enough if I have succeeded in giving you some idea of what the chemist means by atoms and molecules, and how these conceptions help him to explain and understand the intricate and subtle processes of chemical reaction.

## HYPOTHESIS OF RADIANT MATTER<sup>1</sup>

THE enormous literature which has developed from the discovery of radium and from the study of cognate phenomena has made it increasingly difficult to form a calm opinion upon the merits of all the claims which have been advanced, and upon the validity of the theories which have been based upon them. Undoubtedly, the great bulk of the experimental data is exact, although time may show that some of the results which were recorded before the technique was fully developed may require correction. Without questioning in the slightest degree the experiments reported by some of the skillful observers of modern times, one is, nevertheless, permitted to hesitate in adopting hypotheses that not only subvert formerly accepted ideas, but also seem, in many cases, inconsistent with one another.

The chemical world has been accused of accepting too dogmatically the theory of the conservation of matter, the indivisibility of the atom, etc. Ought we not, then, to guard ourselves against a similar fault in adopting newer views?

I propose to take up *seriatim* the methods of reasoning which have led to the present hypothesis of radiant matter as expressed by its chief exponents, and to indicate some points which seem to me to be inconsistent with older views, or in conflict with one another; and I shall begin with what may, from the present point of view, be called a static phenomenon, the behavior of the atom toward light. It is known that Lorentz modified Maxwell's electro-magnetic

<sup>1</sup> Extracts from a review presented to the New York Section of the American Chemical Society at its meetings, November, 1907, and published in *The Popular Science Monthly*, 73, p. 52, July, 1908. Reprinted by permission.

theory of light, by assuming that the vibrations from which light-waves originate are not produced by the atom as a whole, but rather by the vibration of its positive or negative electric charge conceived as a special entity, which we may now personify, as it were, by the more recently coined name "electron." The electron vibrates in an elliptical path which is really the result of two circular oscillations in opposite directions, and of differing amplitudes, but of identical period. An alteration of the radii of these circles would merely alter the shape of the ellipse; but if the *periods* of the two circular motions were made to differ, no single resultant could appear, for the two vibrations would produce waves of different length, i.e., light rays of different refrangibility. Now, a magnetic strain ought to exert some influence on an electron; if it accelerated its dextrogyratory motion, it would retard its laevo-gyration, or vice versa. This is precisely what Zeeman found when he examined the emission-spectra of vapors that were placed in an electromagnetic field; single lines are broken up into two or more finer lines, placed symmetrically with regard to the position of the original one. Righi has generalized the reasoning so that it covers practically every relation between the vibrating electron and the external magnetic strain to which it is subjected, and reaches two conclusions: First, the vibrating electron is electro-negative; second, the ratio  $e/m$ , i.e., electric charge over mass, is about 1000 times as great as the ratio between the electric charge and mass of the hydrogen ion. Assuming, perhaps arbitrarily, that the electric charge is the same, the mass of the electron is about 1/1000 that of the hydrogen ion; it can be no mere coincidence that Thomson, Kaufmann, and others arrive at virtually the same figure for the mass of the corpuscles which carry the negative charges in ionized gases of whatever chemical constitution; in fact, everybody recognizes their identity.

To quote Righi, the neutral chemical atom (as distinguished from the ion) consists of a central mass of positive charge, around which revolve as satellites one or more electro-negative corpuscles, retained in their orbits by some centripetal force.

In connection with this definition, the following points seem to require emphasis: the number of electrons per atom are few, practically corresponding to the valency; this seems to be corroborated by recent experiments of Becquerel on the phosphorescence of uranium minerals at low temperatures, which likewise point out that light-emission is not always confined to the negative corpuscle, as Righi would have it. The total mass of the free electrons in an atom is not sufficient to affect the ratio between specific heats for constant pressure and constant volume of monatomic vapors, like mercury and cadmium; their velocity in their orbits does not approach that of light, and they have no high momentum retained by comparatively powerful internal attractions. These electrons can not be identical with the X-particles which are projected with terrific force from the uranium, radium and other atoms, according to Rutherford and his followers.

I need only touch briefly on the electric discharges in vacuum tubes: it is generally accepted that we distinguish Lénard or cathode rays, which are negative, and positive Goldstein or canal rays within the tube. They can be deflected by electric or magnetic fields, they produce mechanical and heating effects, cast visible shadows, etc., and they behave in general like streams of actual particles charged with electricity. When the cathode ray strikes an impenetrable obstacle, like glass, the X-rays are produced as a secondary effect: these do not behave as if conveyed by neutral particles; have vast penetrating power; contain no electric

charge, as they are not influenced by magnetic or electric fields, and are neither refracted nor reflected. I would emphasize, however, their ability to discharge an electrometer, as well as to influence the photographic plate. Their peculiarities have been recently ascribed to the fact that they represented aperiodic impulses given to the luminiferous ether — which conveys no meaning to my mind, excepting that they can *not* be explained by the undulatory theory. The velocity of the canal rays has been determined, and the mass of their hypothetical particles measured by the amount of their deflection in magnetic fields of varying strength; both values approximate those found for the ordinary chemical atoms or molecules; in the case of the negative cathode rays, however, the velocities and mass correspond to those assumed for the electrons. I confess to a serious difficulty in harmonizing the notion of a corpuscular structure of the atoms with the explanation given by the same school for the need of high vacua for the production of cathode rays. It is said that the electrons must have a considerable free path in order that they may travel with undiminished velocity toward the anode: but if the atoms, instead of being compact elastic bodies, be mere nebulae of electrons, the relation of whose sizes and interstices is comparable to that of the molecules in a normal gas, it follows that a free electron, hurled vehemently forward from the cathode, could pass quite through a number of atoms without collision with any of their constituent corpuscles; the free path of the electron is so enormous, on this hypothesis, that the order of its magnitude could not be materially affected by the degree of rarefaction of the gas customary in the Crookes tube.

We must recollect, however, that the hypothesis, first elaborated by Larmor, that the electrons are the primordial constituents of the atoms, does not, like that of Prout,

simply extend the limits of the divisibility of matter. The electron is not to be considered as a small speck of matter at all, but as a permanent manifestation of energy concentrated on a minute portion of the luminiferous ether. The view and the explanation of many phenomena on such a basis has been acclaimed as the triumph of energetics, the final elimination of the conception of matter. An unbiased reading of J. J. Thomson's Yale lectures, however, will impress anybody that he decidedly *materializes* both energy and ether. Perhaps much of this materialization is purely symbolic, to bring his mathematical reasoning within the comprehension of his audience; but to me it seems that an electric charge which has quantity, mass, inertia, elasticity, and expansibility, which obeys the laws of hydrostatics, and virtually has a surface beyond which it can only produce effects by the medium of mysterious lines of force, has a marvelous resemblance to the picture which the ordinary chemist's mind would form of material substance. His ether is not only that puzzling paradox, at once impalpable and inconceivably dense, rigid and frictionless, which we have accepted as the whole means of explaining the transmission of motion through a vacuum; to extend its importance as the substratum of *all* phenomena it must become heterogeneous and capable of deformation; to form a neutral atom, some of it must become a spherical jelly in which other parts of itself are imbedded as rigid particles. It has, consequently, different degrees of hardness, and is subject to internal attractions. Thomson even volunteers the admission that, for the explanation of certain phenomena, his ether must have structure, or, at least, be stratified.

This can, of course, be no insinuation against the work of some of the greatest living physicists and mathematicians: accepting their premises, I do not doubt that they have

drawn the consequences in the most rigid fashion. I do assert, however, that some of their fundamental terms are used in a different sense from that to which we are accustomed, and that we are, therefore, entitled to doubt whether the conclusions which they reach really affect the phenomena with which the chemist deals: as if one were to discuss the crystallographic structure of Pentelian marble with reference to the architecture of the Parthenon.

A few examples, pertinent to our inquiry, will more precisely establish my meaning. One of the fundamental postulates of Professor Thomson's mathematical argument is the definition of momentum as the product of mass by velocity. Although this is not axiomatic, we accept it as such by reason of the many ballistic experiments which have proved its truth, so long as the projectile's mass was assumed to remain constant: we should hesitate if we were told that mass was to vary, i.e., that a bullet which weighs the same before and after the shot, was heavier during its flight. But the momentum of Thomson's electrons increases faster than their velocity, when the latter approaches that of light; hence, he says, the mass of the electrons increases with their swiftness. True, he calls it an electro-magnetic mass, but some of his followers have forgotten the distinction. At all events, his terms "momentum" and "mass" must not be accepted by us in their usual meaning.

It is perfectly true that Thomson's calculations are corroborated by Kaufmann's experiments on the velocity of radium rays in combined electric and magnetic fields, if the latter's data are calculated according to Thomson's views; without even seeking a radically different basis — which would not be difficult — we can follow Thomson to a point where his departure from ordinary assumptions becomes evident. He shows that the value  $e/m$  diminishes at high veloc-

ities and then he assumes that  $e$ , the electrostatic charge, is constant; therefore  $m$ , the mass, varies. Now, the value of  $e$  is derived from Faraday's law, which would never have been announced if Faraday had not dealt with the equivalent weights as fixed mathematical quantities. In fact, just so far as Thomson substantializes electricity by giving it atomic structure, with invariable mass, the chemical atom becomes wavy and matter evanesces into the ghost-like form which energy has assumed in the chemical mind. If our scientific terms are, as it were, to receive the reciprocals of their present significance — progress may ultimately result, but we should enter into topsy-turvydom with our eyes open.

The electron theory possesses the merit of furnishing a working hypothesis upon which to coördinate the various electrical phenomena of vacuum tube and radio-active origin: chief among which is the increased conductivity of gases. Either direct current measurement or the more sensitive electrometer, determinative of the decrease of electrostatic potential, indicates that gases begin to conduct electricity when affected by ultra-violet light, by cathode and X-rays, by radium, thorium, etc. Ingenious experiments have proved that portions of the gas are positively, others negatively, charged; that they behave as if ionized; the numbers, masses and charges of the hypothetical ions have been measured and found to agree with the assumption that the negative ions have the magnitude of the electrons, the positive ions that of the regular molecules, i.e., the negative ions are always very small and mobile, with the same value for all gases; the positive ions are, at least, 1000 times as large, and vary for different gases. If the gas moves away from the locality of ionizing influence, its conductivity disappears gradually at a rate to suggest reunion of the ions. Plausible, if not quite conclusive, reasoning connects the ionization hypothesis with the

novel phenomenon of the saturation constant; viz., the fact that the flow of electricity through a conducting gas increases proportionately to the voltage between the electrodes up to a maximum, when further increase of potential has practically no effect on the current. This saturation current, it may be remarked, is used to characterize radioactivity; it is admittedly a complex phenomenon, and I should be inclined to lay more stress upon the qualitative than the precise quantitative results obtained in a number of recent experiments.

Those who, like Armstrong, oppose the electrolytic dissociation hypothesis of Arrhenius, naturally attack the ionization hypothesis with still greater vehemence, and I believe that this will be the battleground of opposing theories for some time to come. As the phenomenon is distinctly a secondary reaction, from our point of view, we need not discuss it in its various aspects, beyond noting that even without detectable radioactive agencies the atmospheric air conducts electricity to a slight extent, varying with location, as well as with the hours of the day.

The radiations from the active chemical substances present a very complex aspect; besides light and heat, radium and its congeners send out  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays, respectively electro-positive, electro-negative and neutral when tested in electric and magnetic fields.

From radium  $\alpha$ -rays are sent out about four times as abundantly as  $\beta$ -rays, the  $\gamma$  variety being relatively few.  $\alpha$ -rays are electro-positive, have a speed one tenth of the velocity of light, and a molecular mass of atomic magnitude. They penetrate a few centimeters into air, pass through thin aluminum foil but are stopped by denser metals. As they are but slightly deviable in a magnetic field, their momentum is calculated to be enormous; until, however, better evidence of the total positive charge which they carry has been

obtained, we cannot consider the magnitude of the momentum as definitely established; especially since their speed does not appear to be uniform. From experiments wherein  $\alpha$  particles are allowed to escape freely, and again restrained by a lead cylinder surrounding radium, much of the apparent heat of the latter body appears to be due to the impinging of the  $\alpha$ -rays upon the surrounding surfaces.

$\beta$ -rays are similar to cathode rays; they are less absorbable than the  $\alpha$  variety, and proceed at various speeds, many approaching the velocity of light; they are stopped by solids in proportion to their density.

$\gamma$ -rays are similar to X-rays, of great penetrating power, and they are thought by some to be secondary effects of  $\alpha$ - and  $\beta$ -rays, just as the X-rays originate from the impact of cathode rays on the glass wall of the Crookes tube. Besides, we have a multitude of conflicting accounts of secondary tertiary rays, resulting from these three varieties.

The chief method of research is the study of ionization, with the interposition of screens and magnetic fields, to separate the different kinds of rays. On the other hand, the varieties of rays emitted, their relative strength, and their variations of intensity, are the characteristics upon which the identification of the various so-called transformation-products of radioactive material is based. I have, therefore, copied from Professor Rutherford's book<sup>1</sup> tabulations of these properties.

With regard to these various transformations, we should realize that the majority of the names are titles of hypothetical substances whose existence within certain mixtures is assumed upon the evidence of their momentary radioactivity. The only one really isolated is that emanation which has all the properties of a gas, including that of condensibility

<sup>1</sup> *Radioactivity*, 1905.

at low temperatures — with the exception that its liquid form shows no vapor pressure — but has in addition remarkable energy effects, and has, undoubtedly, undergone transformation in Ramsay's hands. Bearing in mind the infinitesimal quantities of emanation which Ramsay and his associates could obtain, we are alike astounded by their marvelous manipulative dexterity and by the nature of their observations. First we had the gradual appearance of helium, when the emanation was stored by itself; then came the appearance of neon, when the emanation came into contact with water, the latter being partially decomposed into oxygen and hydrogen; lastly the partial reduction of copper nitrate solution, with the simultaneous appearance of lithium, while the emanation underwent a change into argon. The lithium, we are assured, could not be found in the original materials; it represents about .01 per cent of the sodium and calcium found in the same experiment; its actual amount, after correcting a slight oversight in Ramsay's estimate, would be 0.00000003 gram. For such a quantity the amount of copper transformed would be too minute for the detection of a loss from the 0.3 gram of copper which the original solution may be assumed to have contained: but, until a loss of copper be ascertained, to correspond with the gain in lithium, it appears to me that the assumption of transformation is premature. Ramsay found that this solution contained in all 1.67 mg. alkaline chlorides, chiefly sodium chloride; while 0.79 mg. was produced in a blank experiment, when the emanation was excluded. While this latter amount is admittedly derived from the glass bulb, the excess obtained in the presence of emanation is ascribed to the degradation of the copper, neglecting the fact that this second solution must have been fairly acid and would, therefore, have attacked the glass more vigorously. Accepting his suggestion, however, the deficit of copper ought to approach

**TRANSFORMATION PRODUCTS OF THORIUM, ACTINIUM, AND RADIUM ACCORDING TO RUTHERFORD**

Product	Time to be half transformed	Radiations
Thorium ↓ Th. X ↓ Emanation ↓ Thorium A ↓ Thorium B ↓ ?	—  4 days  54 seconds  11 hours  55 minutes	α-rays  α-rays  α-rays  no rays  α-, β-, γ-rays  —
Actinium Actinium X Emanation Actinium A Actinium B	?  10.2 days  3.9 seconds  35.7 minutes  2.15 minutes	no rays α (β and γ) α-rays no rays α, β, and γ
Radium ↓ Emanation ↓ Radium A ↓ Radium B ↓ Radium C ↓ Radium D ↓ Radium E ↓ Radium F ↓ ?	1,200 years  3.8 days  3 minutes  21 minutes  28 minutes  about 40 years  6 days  143 days	α-rays  α-rays  α-rays  no rays  α-, β-, γ-rays  no rays  β- (and γ)-rays  α-rays  —

Active Deposit of Rapid Change  
Active Deposit of Slow Change

0.8 mg., an amount which ordinary analysis can detect. We may, therefore, hope that further experiments by Professor Ramsay will throw light upon this side of the subject.

Of Ramsay's present conclusion, the following résumé may be given: Emanation is a gas of about atomic weight 216.5, derived from radium, of atomic weight 225, simultaneously with  $\alpha$ -particles which are *not* helium. When emanation and the  $\alpha$ -particles are shut up together, the bombardment of the latter breaks up the emanation into helium; but if heavier molecules, like water, be present, they receive some of the bombardment, and the emanation is only degraded into neon; the pressure of copper nitrate still further protecting the emanation, so that it only breaks down to argon. This kinetic explanation is not impeccable; for, according to the principles of mass-action, the preponderance of water molecules in the copper nitrate solution, as well as the predominance of hydrogen and oxygen in its decomposition products, would imply the presence of considerable amounts of neon to accompany the argon. As neon is said to be absent, we must either seek some other hypothesis or explain how the neon reverts to argon after it is once formed.

Ramsay's views contradict those of Rutherford and others, who seek to identify helium with the  $\alpha$ -rays, and the latter would thereby lose a good deal of their substantive character. Furthermore, it is to be noted that the  $\alpha$ -particles bear positive charges: if they were merely chemical atoms, such a charge might possibly be obtained as they tore themselves loose from the larger complex, during radiation; but if they be non-substantive masses of free energy, it will be difficult to reconcile the various assumed transformations with the electro-chemical properties, valencies, etc., of the elements in question.

It must be recalled that Rutherford does assume that the

successive transformations of radium, for instance, are effected by the expulsions of the  $\alpha$ -particles and that these have *atomic mass*: an atom of radium, therefore, contains a finite number of them. As the transformations are atomic and not molecular, Rutherford's application of the mathematics of mass-action can mean but one thing: that the various rates of transformation depend upon the chances of encounter and relative positions of the particles *within* the atom. These rates, however, as measured by the period of decay, vary from thousands of years to a few seconds for the different educts, and that irregularly in the order of transformation — such great differences could only be explained by an infinite number of components, with large free paths,—in other words, electrons. It would then remain to be shown what caused a certain great number of negative electrons to form an electro-positive  $\alpha$ -particle, and become expelled with great violence from their surroundings.

Naturally, the failure of an hypothesis to explain certain facts does not invalidate the latter. Rutherford's brilliant analysis of the curves of increasing and decreasing ionization and the agreement observed with calculated results prove that he is not dealing with mere fortuitous coincidences. Many of his conclusions seem incontrovertible upon his premises; but here again, the *advocatus diaboli* must step in and ask whether the premises are axiomatic: two of them appear to me to be doubtful. (1) A curve of decay is based on electroscopic measurements upon the tacit assumption that the rays sent out by that particular phase are always the same; but we are told that both  $\alpha$ - and  $\beta$ -rays vary greatly in speed and momentum, hence neither variety would show a uniform ionizing power; assuming that a substance did send out  $\alpha$ -rays for a long time, but that their velocities were gradually reduced, would not the ionization indicate a more rapid decay

than was really the case? (2) It is practically assumed throughout that ionization is directly proportioned to the amount of radio-active material present: but this remains to be proved. Where layers of any density are involved, we know that it is not true, owing to internal absorption, etc.; for ideally thin layers, weighing and other measurement are out of the question.

I do not think that this latter objection ought to be dismissed lightly, when we find such a phenomenon as the almost universal ionization of the atmosphere ascribed to the presence of radium or its educts. Thomson himself has shown a variety of ways for ionizing air, when any variation in the amount of radium present — or, rather, absent — is out of the question; some of these serve particularly well to explain the phenomena in the open air. Recently, indeed, quite a number of investigators have observed diurnal variations in this atmospheric ionization, sufficiently marked to require some other explanation than the production of emanations from the earth or surrounding materials. Gustave Le Bon, in his "*Evolution de la Matière*," shows how the gold-leaf electroscope is discharged when connected with some very dry sulphate of quinine, which is taking up hygroscopic moisture. Are we ready, with him, to assume that the quinine is catalyzing some atoms into Nirvana, or that the electroscope may indicate many changes that are not intra-atomic?

## REPORT OF THE COMMITTEE OF THE OVERSEERS TO VISIT THE CHEMICAL LABORATORY OF HARVARD COLLEGE

TO THE BOARD OF OVERSEERS OF HARVARD COLLEGE:—

Your Committee beg leave to report that they visited the Chemical Laboratory on Tuesday, March 9th, 1909, and were received by Professors Jackson, Sanger, Richards, Torrey, and Baxter, and Dr. Henderson. At the opening of the meeting an expression of deep regret at the recent death of Dr. Wolcott Gibbs, Professor Emeritus and distinguished chemist, was recorded. After the reading of reports on the present condition of the building, and some discussion, the Committee were shown over the laboratories.

The condition of the laboratories in Boylston Hall has been so fully set forth in previous reports that it seems now hardly worth while to repeat in full the criticisms as to their condition, which have been so repeatedly made. It may be, however, of advantage on this occasion to refer to one or two points of pressing importance. The needs of those desiring to study chemistry at this University may be divided into two classes: first, the needs of the undergraduates, and, second, the needs of those conducting research.

So far as the undergraduates may be concerned, the most pressing necessity at the present time is for the better accommodation of students in qualitative analysis. The space assigned to this work has been so inadequate that additional accommodations have been found for the students in the west wing and basement of Dane Hall. For those who are working in what is now termed Chemistry 1, there is such

imperfect accommodation that about half of the students have been forced to carry on work in the unsanitary cellar, now called Room A. There is no space anywhere for laboratory instruction in elementary organic or in technical chemistry.

Turning now to the needs for research: For organic research the accommodation is fair, but not ample or comfortable. For inorganic and physico-chemical research the facilities are very bad, and for technical research there are no facilities at all, nor is agricultural, sanitary, or biological chemistry at all provided for in Cambridge.

In precise investigation of atomic weights, Harvard probably leads the world. Such work demands well-ventilated rooms, free from dust and noxious vapors of all kinds, — for these may ruin the purity of the substance to which months of care have been devoted. Researches in physical chemistry need rooms of constant temperature, free from vibrations and changes in electrical field. This work is now so badly provided for that it is greatly hampered.

The lecture-rooms, which for the most part were designed at the time of the first occupancy of Boylston Hall in 1857, are now not only inadequate for the number of students to be accommodated, but are lacking in ventilation, and are too few for the proper preparation of experimental lectures.

One of the most important needs at the present time is a better provision for the administration of laboratory and storeroom, — a very important feature in the economical carrying on of a well-conducted laboratory.

When the present building was built, there were about one hundred students in the required lecture and recitation course, but few laboratory students. The number of the latter steadily increased from time to time, and the other departments of the University which also found room in Boylston Hall

were gradually crowded out, until in 1900 every nook and corner in the building which could be utilized had been exhausted. The consequence was that when over six hundred men applied for desks that year there was a waiting list of forty men. This continued for several years, and the University was in the position of not being able to make good its announcements concerning chemistry. With this overcrowding, a steady deterioration has taken place in the equipment of the building, and the result is that many men are now deterred from taking the elementary course in chemistry on account of the known conditions of the laboratory. It is also probable that many students do not go on with advanced work on account of the unfavorable conditions under which they have to work.

It has been suggested that the present building should be entirely refitted internally, but its arrangement at the present time is so entirely unadapted to alterations of any kind that it would be necessary to tear out the whole interior of the building, and even then it is not probable that a satisfactory arrangement of a new set of laboratories and lecture-rooms on a modern basis could be planned within its four walls, as careful measurements of Boylston Hall show that the available space within the walls would not be adequate for the needs of the department if the building were to be remodeled. A further use of Dane Hall, aside from the obvious inconvenience of two separated buildings, would not give sufficient room for expansion. In short, any remodeling or enlarging of present quarters would be but a makeshift. For this reason it was borne home strongly to the members of the Committee as it has been for a long time to the members of the teaching staff, that these needs can be met in an adequate way only by the construction of a number of new buildings,—the separate buildings being devoted to different branches of

chemistry, and placed not far apart, to be connected with each other by a central Administration Building. The latter might contain also the chief lecture-rooms, a chemical museum, as well as a library, and other facilities to be used in common by all; separate buildings, as has been stated, to be devoted to the different branches of chemistry. One could be devoted to organic and industrial chemistry; a second to inorganic chemistry; a third to physical chemistry, and a fourth to quantitative and qualitative analysis. Portions of one or more of these buildings could be set aside as research laboratories, of their respective kinds. In this way provision would advantageously be made for the adequate separation of work injurious to other parts, either because of noise, vibration, or noxious gases; on the other hand, connection with the central Administration Building would promote unity of interest.

Preliminary sketches of several ways in which these buildings might be arranged were shown to the Committee. Such a scheme of a group of buildings devoted to chemistry would necessarily demand considerable space of ground, but the Committee understand that land for this purpose is available in Cambridge in a situation which would not only be well adapted to the purposes of the buildings erected upon it, but would enable them to become an ornamental addition to the various groups of buildings now in the University grounds.

Such a proposed radical departure of the administration of the Department of Chemistry would undoubtedly involve a large expenditure, but when we consider the importance of the subject and the character of the teachers and investigators who are interested in this department of science, we do not hesitate to recommend most urgently that steps be taken in order that a beginning may be made to work out an entirely new foundation for this department.

With the immense development of the various departments

of science which has taken place since the chemical department was first established on its present basis, attention has been so acutely drawn to other fields of labor that the public has failed to grasp the important rôle which has been played by pure chemistry in almost all of the departments of industry and science which have contributed toward the advancement of the material prosperity of mankind. It seems proper, therefore, to call attention at this time to the rôle which chemistry has played in this great awakening of science in its application to humanity.

In the first place, in this age of steel, much depends upon the chemical manufacture of the various kinds of hardened iron. As iron does not occur in commercial quantities in a native state, the preparation of all the enormous quantity which is used depends entirely upon making a sufficiently pure product by a method which avoids unnecessary waste. Both the elaboration of the method and the determination of the purity of the material can be accomplished only by trained chemists; moreover, the protection of the finished product from the chemical change of rusting lies also in the same hands. When one takes into consideration the fact that steel serves not only a chief rôle in the construction of ships, bridges, and buildings, but also is concerned in the manufacture of almost every article which we use, because of the need of steel tools of suitable quality, one can see how great an indirect part chemistry plays in every act of our life. Indeed, all the building materials of the future, such as the composition of concrete, and the manufacture of glass and of pottery, present at the present time chemical problems of enormous interest.

Another great industry, the soda industry, is, of course, wholly chemical, and so is the soap industry, which depends upon it. Before chemists had shown the world how alkalies

could be made on a large scale, these all important substances were to be obtained only from the ashes of wood and of seaweed. The consequence was that both soap and glass were very expensive, and the result to the growth of civilization was lamentable. The cleanliness, and therefore the health, of the world is due to Leblanc, and since then to Solvay, two chemists who have made soap cheap enough to replace the mediæval perfumes which were made to conceal the dirt.

The two great departments of applied biological chemistry are medicine and agriculture, and it is only now that systematic and hopeful attempts are being made to apply chemical knowledge broadly in these fields. Already there can be no doubt that progress in this direction in the next few decades will be enormous. It has been arrested during the last five or six decades because pure chemistry, after developing for years in connection with medicine and agriculture, found itself at a point where it had to turn to a systematic development of its whole field. Now, however, this development has gone on so far that much can be done with our present knowledge of organic chemistry and physical chemistry, and much more will be possible in the future if this development of pure chemistry goes on with the same acceleration as in the past.

For the welfare of the human race, it is essential that this acceleration should continue, and there is no loftier public service than advancing these activities. The advantageous results of dealing scientifically with such subjects are to be found everywhere in health and comfort, in relative freedom from pain, in increased immunity to disease, so far as medicine is concerned; in greatly lessened labor and enormously increased efficiency of labor, resulting in wonderful increase of productivity, and general economic amelioration for scientific agriculture.

In the industries in which fermentation is a problem to be dealt with, individual chemical research plays an important rôle, and it was while pursuing such investigations that Pasteur discovered the great rôle of bacteria, revolutionizing at the same time the whole domain of another department of science, — medicine.

In agriculture we find a striking example of the value of pure science, for here it was that the investigations and experiments of Liebig clarified and simplified the subject.

The fertility of the earth depends upon the chemical manures, and it is calculated that in thirty years the present source of nitrogen (Chile saltpetre) will be exhausted. The loss of nitrogen in combustion, and otherwise in civilization, is a permanent one. Chemical means exist for getting it back from the air. With power from electricity producing a high temperature, we can get nitric acid from the air, so that the danger of giving up intensive agriculture from lack of nitrogenous manure has been averted by chemistry.

The chief product of farming is starch, which forms the bulk of all edible vegetables, for that is the chief food of man, and in a larger degree it is the chief food of the herbivorous domestic animals. The amount of starch which is consumed as food by man and the domestic animals in the United States alone cannot be far below fifty million tons per year. In addition to this enormous use of the substance, great quantities of it are being converted into glucose and into alcohol, and the use of starch for these purposes as our scientific technology develops in this direction, promises to be far greater than at present. We may, indeed, expect that glucose will largely replace cane sugar, and we are now assured from our present improved devices that alcohol may be, at need, substituted for coal and the products of petroleum in the production of heat and

power. The technology, then, of an inconspicuous substance, if we may use the term, such as starch, becomes at once one of the greatest problems in the whole field of economics, the proper treatment of which depends upon the past achievements in the field of pure chemistry and progress to come in that field.

The development of paper from wood pulp is now a source of great danger to our forests. The question of getting pulp from straw and cornstalks for this purpose becomes, therefore, an important one, in the solution of which the prosperity of the country is intimately involved.

The improvements of our textile fabrics, such as the manufacture of artificial silk, have great possibilities for advancement.

All the new processes for reproducing photographic pictures are largely chemical problems, as are also coinage, chemical assaying, and the whole domain of metallurgy.

Coming now to the medical side of the question, we see at once that the science of nutrition and the value of every different kind of food in the maintenance of health, and its adaptation to disease, are all chemical problems, which are becoming topics of increasing interest to those who are assisting actively in the advance of practical medicine. The actual control of the food supply is largely chemical, and the pure food laws can be enforced only through chemistry.

Of the many applications of chemistry to medicine, the problem of immunity in its broadest sense is perhaps one of the most important, and then we have also the problem regarding those diseases which are in the largest sense systemic,—like diabetes, gout, and some of the atrophies, and even senility itself. It is possible even that the question of the origin of cancer, one of the few diseases which has thus far baffled research, and which so far as we know is probably not

of microbic origin, may turn out eventually to be a purely chemical problem.

The whole domain of hygiene and preventive or state medicine is a field of investigation which only those well trained in chemical research can deal with intelligently. A chemical training is, therefore, an essential part of the education of the health officer, who plays so increasingly important a rôle in the economy of our modern civilization.

It is hardly necessary to maintain at length here the boon to humanity which such chemical substances as ether, chloroform, and cocaine have been, and the important rôle which many of the coal tar products have played in pharmacology.

The law against arsenic in wall-papers was the result of a movement which was started from the University Laboratory, being put on a scientific basis by Professor Sanger's proof that arsenical wall-papers were injurious, by analyses of the urine of patients. The debt which surgery owes to this University for the part it played in the introduction of ether as an anesthetic in surgical operations should not be forgotten.

The structure of many physiologically active substances has now been made out, and by making allied substances with similar structure, by an experimental transposition of molecules in the hands of trained workers, many new and equally valuable drugs may be obtained. This scientific search for medicine, which is still in its infancy, is sure of bringing great results in the future.

Finally, from a purely business point of view, the encouragement of chemical research is of the highest importance. As competition increases, the successful man will more and more be the one who lets nothing go to waste, but adopts the most efficient processes and devises new ones still more efficient;

who works up his by-products into some useful, and, therefore, valuable substances, who economizes energy, whether this energy comes from coal or water power, or human labor. The field is too large and chemical laws too complex to have the results come accidentally. They can be accomplished only by a systematic investigation of the whole field of chemistry. Only upon the study of pure chemistry and the laws which underlie it, can be built the practice of chemical technology, just as our whole modern technique of electricity was built upon the purely scientific experiments of Faraday, or the modern system of wireless telegraphy was built upon the calculations of Clerk Maxwell, and the scientific experiments of Hertz. An improvement of a chemical process which betters the yield by five per cent may mean \$10,000,000 a year to a single large corporation in a time not far distant, if not even to-day.<sup>1</sup> Colossal fortunes have already been made in this way. It is slowly creeping into the minds of business men and manufacturers, that a trained chemist can improve an output or effect economies, and that something more than a mere analyst is necessary in a manufacturing concern. But how many persons understand that chemistry is essential in most plans for the social uplifting of the people?

In Europe it is a truism that well-endowed and active laboratories of pure chemistry are a source of wealth to the community, and nothing is more striking than the close co-operation between the German chemical professors and the "works-chemists" of the great German chemical industries. This coöperation it is which has put the German chemical industry at the head, with no other country a respectable second. England is fast losing her supremacy in manufacturing where chemistry plays a part, and the success of the

<sup>1</sup> The gross income of the Steel Corporation in 1907 was \$757,000,000; its net income available for sinking funds, interest, dividends, etc., was \$160,000,000.

Germans and the backwardness of the English is to be attributed to the difference of the educational systems of the two countries, in the large supply of highly educated chemists in Germany, and the smaller supply and want of their employment in England. In a very large degree, the commercial prosperity of the German Empire is dependent upon this supremacy. The German Emperor himself has said this, and it is generally believed in German universities. The Badische Anilin und Soda Fabrik employs more than one hundred men on pure research, and other corporations in proportion, not only for purely chemical work, but for the manufacture of iron and steel, and in other kinds of industry.

There are two chemical plants in Germany, each as big as the General Electric Company's plant, whose works are so correlated that the waste products of one serve as the valuable products for the other. From one to two hundred doctors of philosophy in chemistry are employed in some of these great establishments.

The importance of chemistry on the continent of Europe is attested in a remarkable manner by the expenditures of the several governments for the equipment and maintenance of the chemical laboratories of their universities and schools of technology. In Berlin, for example, the cost of a laboratory built about twelve years ago for Fischer, was 1,316,000 marks, with 64,000 marks more for a connected dwelling-house for the director. There are in Berlin, in addition to this laboratory, laboratories of inorganic chemistry and of physical chemistry for the university, and a fine large chemical laboratory for the technical school. All these laboratories together probably cost a good deal more than 3,000,000 marks.

Strassburg is a university with about one third as many teachers and students of chemistry as Harvard. The Strass-

burg laboratory is devoted to organic and inorganic chemistry exclusively. To build it to-day in Cambridge would cost about \$300,000. Allowing for difference in cost of construction, either of these cases indicates that the Prussian government would, in a case like Harvard's, devote about \$1,000,000 to the construction of chemical laboratories.

Not less significant are the yearly budgets of some of the European universities. In Berlin the chemical laboratory above mentioned has from the government 80,000 marks a year for running expenses, the physico-chemical laboratory 20,000 marks. These sums are in no part derived from tuition fees, but are direct subsidies. Together with the similar appropriations for the other chemical laboratories of the university and the technical school they certainly exceed 150,000 marks yearly.<sup>1</sup>

In Berlin the physical laboratory receives 33,000 marks a year. The university library has 121,000 marks, which is not more than three fourths the sum devoted to all the chemical laboratories of the university and the technical school, and only fifty per cent more than the sum devoted to one of them.

In Leipsic the three chemical laboratories have 80,000 marks a year for running expenses, the physical laboratory only about 27,000 marks.

In Strassburg the chemical laboratory has 34,000 marks a year, the physical laboratory 14,000 marks; the library, which serves both university and province (Alsace-Lorraine), has about 72,000 marks. If one assigns one half of this library budget to the university and one half to the province, it appears that a chemical laboratory which is dealing with only two of the important divisions of chemistry and has but one

<sup>1</sup> The Harvard laboratory has from the Corporation approximately \$900 yearly for running expenses. Other sources of income are similar in the two countries.

professor ordinarius, and but one professor extraordinarius, receives nearly as much money as the university library for running expenses.

In Zürich the university chemical laboratory is voted f.24,800 a year. This sum is approximately equal to the total yearly appropriations for the laboratories of physics, botany, zoölogy, anatomy, physiology, and pathology together (f.25,600).

These facts indicate that a German or Swiss government would, in a case like Harvard's, devote about \$25,000 a year to the maintenance of chemical laboratories. These data, together with the confirmatory facts, also indicate that in Germany and Switzerland the chemical laboratories are regarded as of equal importance with the university library, about three times as important as physical laboratories, and as equalling in importance the institutes of six other sciences taken together.

Speakers at meetings in America which have any bearing on chemistry intimate that we are beginning to profit by this lesson, and are using trained scientific knowledge in ever increasing proportion, and that the results can be already seen.

The General Electric Company employs from twenty to twenty-five physicists and chemists, and the Eastman Kodak Company, which is highly successful, employs three or four research chemists. The Pennsylvania Railroad has a large staff of chemists assisting their research chemist in studying the qualities of steel.

If we admit as a principle that the funds should be distributed to each department of the University in due proportion, then we think that the claims of the Department of Chemistry should stand very high. Harvard has always been a leader in university education in this country, and it is still aiming

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strenuously to maintain that position. Is it not wise, therefore, in planning the education of her students, to give due encouragement to the distinguished staff which is now laboring under exceeding difficulties to maintain a well-earned supremacy in this department?

Is it not advisable that Harvard should recognize the new movement of industrial chemistry? Should she not be a leader in this line of research, and come thus in close touch with the wants of the people by showing them how to make production more effective? By following the policy already adopted by some of the state universities and giving instruction in agricultural chemistry, it is not too wild a dream to hope that the abandoned farms of New England may be blossoming like gardens in the next fifty years.

Your Committee do not, therefore, hesitate to indorse the plan already outlined by this department. It is estimated that buildings of the character contemplated can be built for \$500,000; a further sum of \$500,000 would be needed for the proper endowment of such a plan. This is in itself doubtless a large sum, but small in comparison with amounts expended on many industrial projects.

Although it may not be possible to carry out this scheme at once on the scale contemplated, the establishment of a research laboratory as a beginning would be of great benefit, if the project could be carried out on a consistent plan, which should be adopted at the outset. The estimates for such a laboratory have been made, and in round numbers would amount to about \$50,000 for building and installation. A further sum of \$50,000 would be needed for endowment.

The Committee would, therefore, urge strongly that an attempt be made at once to obtain \$100,000 for this purpose, and thus make a beginning of the development of this

department on a scale suited to its needs at the present time.<sup>1</sup>

The last century has been a century of mechanical power, made available by the perfection of machinery and the development of electricity. The coming century promises to be a chemical century. Should Harvard, if all this be true, be content until it has obtained the best chemical laboratory in the world?

J. COLLINS WARREN,  
CLIFFORD RICHARDSON,  
JAMES M. CRAFTS,  
MORRIS LOEB.

March 27, 1909.

<sup>1</sup> Within a month from the date of this report Professor Loeb and his brother James Loeb generously carried out the Committee's recommendation by offering \$50,000 for the proposed building, provided that other friends of the University should subscribe an equal sum. The project is now completed, and the research laboratory, named the Wolcott Gibbs Memorial Laboratory through the suggestion of Dr. Loeb, is now in full operation. [*Editor*, April, 1913.]



WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY



## THE CONDITIONS AFFECTING CHEMISTRY IN NEW YORK<sup>1</sup>

IN assuming the chair, I am confident that the coming year will be one of great progress in our section's history, not through any merit of its officers, but through the ever-increasing spirit of coöperation among the members, and the rapid strides which research and industry are making in this country. You will hear reports, this evening, of two important general meetings of interest to our membership, that of our own society at Detroit and that of the International Congress of Applied Chemistry at London. In both, members of this section bore a worthy share, and it is a gratifying tribute to American progress in science and industry, that the International Congress chose America for its next meeting-place. It is not only the foreigner who lands at Ellis Island that deems America synonymous with New York, and the members of this section must be prepared to do their full duty, during the next three years, in order that our foreign brethren may carry back from their visit a crystalline rather than a colloidal vision of chemistry in America.

And so, gentlemen, I have preferred to devote the minutes which custom permits your chairman to employ in airing his personal views, to a survey of the conditions affecting chemistry in New York, rather than to the presentation of some debatable scientific ideas, as I had originally intended. The choice of the more subjective topic is rendered more appropriate by the fact that this meeting is to be followed by a

<sup>1</sup> Address of the chairman of the New York Section of the American Chemical Society, delivered October 8, 1909. Reprinted from *Science*, N. S., 30, No. 776, pp. 664-68, November 12, 1909.

session of The Chemists' Club, called for the purpose of settling a question vitally affecting the interests of New York chemists.

Eighteen years ago, when the men who had carried the American Chemical Society through so many vicissitudes organized this section, in order that the general society might become a truly national one, I had the honor, rather than the duty, of being the first local secretary. The meetings were so poorly attended, the original papers so scarce, and the general business so unimportant, that no heavy work devolved upon its officers. We met in the chapel of the old university building, where Professor Hall and I had our primitive laboratories, out of which we carved, with some difficulty, shelf-room for the fragmentary society library. When we felt in need of a little variety, we sat in Professor Chandler's lecture-room in 49th Street and listened to the passing trains; or in East 23d Street, peered at the chairman ensconced behind batteries of Professor Doremus's bell-jars and air-pumps. An attendance of forty members, I believe, was a record-breaking event.

I need hardly expatiate upon the wonderful changes that have been wrought since 1891. Our three colleges have moved far uptown, and the splendid Havemeyer laboratories of Columbia and New York University, and the beautiful new chemistry building on St. Nicholas Terrace, make us glad to miss the dingy and crowded places where chemistry was taught an academic generation ago. Our own section and kindred societies have been meeting in this hall of The Chemists' Club for the past ten seasons, and no one can estimate what share a fixed and commodious meeting-place has borne in the marvelous increase in membership and attendance. The other important factor is, of course, the growth of chemical industry in this vicinity.

While we can, therefore, congratulate ourselves upon the great strides that have been made, during the past two decades, it behooves us to inquire whether there are not still some drawbacks to our progress, not by way of carping criticism, but for the purpose of seeking such effective remedies that future progress may be made absolutely certain.

For obvious reasons, we need not ask whether the internal conditions in the chemical factories are satisfactory; since there the managers must know that their success depends upon the scientific abilities of their chemists. It is doubtful whether the same can be said of the establishments which employ a chemist or two to apply specific tests; and it is certain that there are still many factories which conduct, by rule of thumb, operations that should be continually controlled by scientific tests, if shameful waste is to be avoided.

The American people are but slowly learning the importance of the educated banker and the expert accountant alongside the brilliant financier and the bold speculator; similarly, while they acclaim the clever inventor and the skillful engineer, they have yet to recognize the worth of that expert accountant of material economy, the industrial chemist. Quite aside, therefore, from any wish for greater profits to our associates who are gaining their daily bread as commercial or analytical chemists, patriotic motives lead us to the earnest hope that closer watch upon the economy of production may bring about that conservation of natural resources of which the politicians prate, but for which the chemist works. How, then, can the status of the independent commercial chemist be raised in our city? By giving him a central rally-point; a home that proves to the layman that his is a skilled profession, not a mere job-hunting trade; a place where the manufacturer or merchant can find the man he wants without a rambling search through the city directory. Doubtless, some

of our colleagues are so well known, that all the business comes to them which they can handle. But the many additional independent chemists, whom our commercial situation demands, can only establish themselves if they can secure proper laboratory facilities, without hiring attics in tumble-down rookeries.

Every year scores of New Yorkers graduate in chemistry from our local institutions and return from years of protracted study in other American and European institutions. They are enthusiastic for research; in completing their theses they have laid aside definite ideas for subsequent experimentation; but they have no laboratory. While waiting to hear from the teachers' agency where they have registered, while carrying on desultory correspondence with manufacturers who *may* give them a chance, they do not venture upon expenditure of time and money to fit out a private laboratory, which they may be called upon to quit any minute upon the appearance of that desired appointment. Often necessity or tedium will cause them to accept temporary work of an entirely different character and indefinitely postpone the execution of the experiments which they had mapped out. Who will estimate the loss of scientific momentum, the economic and intellectual waste, which this lack of laboratory facilities for the graduate inflicts upon New York, as compared with Berlin, Vienna, Paris, and London? Either our universities and colleges, or private enterprise, should provide temporary desk-room for the independent research chemist.

So much for the purely practical side of our question. How about the opportunities for presenting the results of investigation? We all appreciate the excellence of the three chemical journals published by our own society, as well as that of the Society of Chemical Industry, and we may say that these, together with the independently conducted peri-

odicals, enable everybody to obtain a hearing; but it does seem to me that the cost of subscribing to all of these journals is excessive, and that much unnecessary expense is incurred through duplication of administrative efforts, as well as through duplication of abstracts, etc. This, of course, is a problem with which we, as a local section, are not directly called upon to deal; nevertheless, it is proper to call the attention of those who are interested in the management of chemical societies in America to the fact that membership alone in the various chemical organizations of New York costs upwards of fifty dollars per year, and that it would be but fair to so arrange matters that the total cost would be reduced by a sort of clubbing arrangement, proportionately to the number of societies to which a member belongs. It seems to me, however, that in one particular point we are at a distinct disadvantage as compared with the foreign chemists: the frequency of regular meetings at which papers can be presented for the purpose of securing priority of publication. Would it not be possible for our various local sections, including the Chemical Section of the New York Academy of Sciences, to arrange the dates of their meetings conjointly in such a way that a meeting would occur once a week during nine months, and once a month during the summer, thus securing for the New York chemist the same opportunities for the early presentation of a scientific discovery that are possessed by his brethren in European centres? There is, of course, another remedy which appeals to me, though I do not express it with any degree of urgency; namely, the consolidation of all local sections into a single organization which would affiliate its members automatically with all the national bodies now in existence, and would turn over the scientific material of its meetings to those journals for which it seemed most suited. As a matter of fact, glancing over the annual lists of

our various local organizations, I find a remarkable interchangeability of officers, and can hardly imagine that the interests of their memberships can be very far apart if the chairman of the New York Section of the American Chemical Society in one year is the next year expected to guide the fortunes of the New York Section of the American Electrochemical Society or of the Society of Chemical Industry. If this were done and we could then exert our influence upon the various general societies to avoid duplication of work, by issuing their chemical abstracts jointly, the strain on the purses as well as the shelves of American chemists would be greatly relieved.

There is still another point, however, in which the American chemist is at a great disadvantage as compared with the European: the ease of securing material for his research and of comparing his results with those of others. In Europe, especially in Germany, research is never seriously delayed by lack of a needed preparation, whereas none of our supply houses carry a full stock of chemicals. To obtain a single gram of some particular substance, needed for a few preliminary tests, frequently causes weeks of delay, as well as the disproportionate custom house and brokerage expenses involved in the importation of small quantities. Besides, owing to the better centralization of scientific laboratories in Europe, and the existence in each case of a fairly complete set of specimens accumulated in the researches of large numbers of academic investigators, it is comparatively easy to obtain by correspondence research material or typical specimens for comparison. In this country, on the other hand, laboratories are scattered throughout the numerous colleges and universities, and there are no established rules by which specimens must be deposited with the laboratory. In smaller laboratories, especially, the chances of preservation after the

departure of the investigator are not very good. It would be, consequently, very much more difficult to obtain such specimens here. I would suggest, therefore, that a chemical museum be established in New York, to perform for the American chemists the functions that the Smithsonian Institution so admirably carries on for the benefit of American naturalists. This museum would not attempt to be a popular show-place, but would embody, in the first place, as complete a collection as possible of chemically pure materials of the rarer kinds, so as to supplement, but not in any manner compete with, the stock of commercial supply-houses. Any scientific investigator would be entitled to borrow or purchase material required for immediate experimentation, and all used articles would be replaced as quickly as possible.<sup>1</sup>

In the second place, it would be the depository for specimens of new substances obtained in American research. Every chemist would be invited to send to the museum a small quantity of each substance newly prepared by him, not, indeed, as an evidence of the good faith of his investigation, but, rather, to enable future workers to obtain such material, either for comparison, or for further experimentation with the least possible delay. Many substances that are now carried away from universities by students who subsequently abandon chemical research, or which belong to the families of deceased chemists who do not know what to do with them, would thereby be rescued from oblivion, and might ultimately become of the greatest value for a special purpose.

Thirdly, this museum would invite chemical manufacturers to send standard samples of their products, and thereby facilitate the commercial relations between consumer and manufacturer.

To such a museum there could be attached a competent

<sup>1</sup> A museum of this kind was provided for in Dr. Loeb's will. [EDITOR.]

staff of workers for the preparation of samples not otherwise available. In the analysis of samples submitted as official standards, we should have the beginning of that *Chemische Reichsanstalt* which is now the chief object to which German chemists are directing their attention.

The past twenty years have seen the construction of innumerable teaching laboratories in our vicinity. They have seen an undreamt-of development and growth of chemical industry, and, above all, they have seen the coming together of the scattered chemists into a large and powerful society. Now is the time when we should make every effort to direct these forces that we have marshaled toward the attainment of definite objects, and coördinate all our enterprises in those directions that will make for the improvement of the intellectual as well as the material conditions of our beloved city.

## SIR ISAAC NEWTON<sup>1</sup>

WE celebrate so frequently the heroic deeds of warriors that it may be a welcome change to spend a short hour in the consideration of a great man whose renown depends entirely upon peaceful victories. Isaac Newton was a farmer's son, who lived a quiet life of eighty-five years almost entirely unaffected by the events of the world about him, but who left, nevertheless, monuments as important as those which commemorate any victory on land or sea. He fought and conquered ignorance and error; he established new laws of thought; he discovered for us new beauties in nature; and he opened before our eyes the harmonies of light that are as wonderful and as elevating as the harmonies of music. Unselfish and regardless of worldly gain, he succeeded in adding untold wealth and comfort to our common store. Mathematics, astronomy, navigation and mechanics all owe a mighty debt to this quiet student; and in Westminster Abbey his monument is well placed among England's heroes of thought and action.

Sir Isaac Newton's name means something to every one of us; but I doubt whether the majority of this audience would be able to indicate exactly his claims to fame, and you may be glad to have some of them pointed out.

He was born at Woolsthorpe, in Lincolnshire, on December 26, 1642,—the year of Galileo's death. His father, Isaac, he never knew, and he was brought up by his mother, Hannah Ayscough, and her brother. He was educated at Gran-

<sup>1</sup> There is no clue on the manuscript as to where this lecture was delivered. It was evidently intended for a popular audience having little knowledge of science. Marginal notes show that it was illustrated by experiments and lantern slides.

[EDITOR.]

tham Grammar School, and in 1657 he returned to his mother's farm; but he cannot have been a very successful farmer, since he was described as a very dreamy boy, and always prone to study. Four years afterwards, by his uncle's advice, he entered Trinity College, Cambridge, and very soon made his mark as a mathematician. It was just at this time that a great advance inaugurated by Descartes, the application of algebra to geometrical calculations, was arousing the interest of mathematicians. Stimulated by this, young Newton developed a still grander advance by the discovery of the method of infinitesimals.

His study at Trinity College was interrupted in 1665 by the appearance of the plague in Cambridge, and he took refuge at Woolsthorpe. A somewhat doubtful but well known legend reports that here, in the summer of 1666, while he was lying under an apple tree and ruminating upon some mathematical question, a falling apple drew his attention to those phenomena which he later elucidated through his law of gravitation.

In 1667 he returned to Cambridge as one of the governing board of his college, and two years later, at the age of twenty-six, he became Lucasian Professor of Mathematics, and lectured chiefly on optics, in which branch of physics he made some of his most remarkable discoveries. From that time on his life was a continuation of successes. In 1672 he was elected to the newly founded Royal Society, practically the oldest society for scientific research in the world, of which he became President in 1703. In 1687 he published his *magnum opus*, entitled "Philosophiæ Naturalis Principia Mathematica." He was elected to Parliament in 1689, and served for many years. In 1694 he was appointed Warden of the Mint, and in 1697 Master of the Mint; and since his time it has been the custom to entrust the British Mint to some master of

physical science. As a result I believe that the London Mint has always been foremost in the application of scientific processes to the problem of securing permanent and stable coin for the realm.

In 1705 Isaac Newton was knighted by Queen Anne, and in 1727, on March 20, laden with all the honors which his country could bestow upon him, he died peacefully, mourned by all, hated by none. He was buried with all honors in Westminster Abbey, and a fitting monument was erected over his grave.

His character is said to have been of the kindest, and all contemporaneous records speak of his amiability. A patient student, a keen observer of nature, and a brilliant inventor, he stands out through his work as one of the greatest scientific men of all time. His great services to mankind embraced discoveries in mathematics, astronomy, and physics. Perhaps his mathematical work ought to be considered the most important, for it might be considered to be at the root of all our scientific knowledge, and yet I despair of explaining to you in what these mathematical discoveries consisted. Up to his time it was only possible to calculate with quantities that were not supposed to change during the calculations. He showed us how to work with quantities that varied. Before him it was necessary to imagine bodies to be at rest before their relations could be ascertained; he showed how to deal with moving bodies. His invention "Fluxions" (now called the "Differential Calculus") was for the mathematician what the Röntgen discovery is for the physician. The fact that Leibnitz almost at the same time independently made the same discovery, does not detract from Newton's merit.

Having devised this great improvement in calculating he began to see clearly things that Copernicus, Kepler, and Galileo had vainly attempted to comprehend. Perhaps the

earlier investigators had actually understood these things in part, but not clearly enough to explain them to others. For example, there were several ideas of Galileo's about motion which Newton has made so clear to us that we now call them Newton's Laws, namely:

**First Law:** If no force acts upon a body in motion it continues to move uniformly in a straight line. Formerly men imagined that a body must be continuously pushed to keep it moving. Now we know that force is needed to stop it. Ordinarily the force applied is friction, but if a body moves with little friction over a smooth surface, as in skating, a single push causes it to travel a long distance.

**Second Law:** If force acts on a body it produces a change of motion proportional to the force and in the same direction.

**Third Law:** When a body exerts force upon another body it experiences an equivalent reaction from the latter.

The results of these laws were long known, but the principle was not understood. When David killed Goliath, as we read in the Bible, he shot a little stone at him from a sling. He knew that if he swung the sling around, the pebble would be held back by the sling that only allowed it to go a certain distance from his hand, but as soon as it was released it did not fly in a circle, but in a straight line. Here we have Newton's first law; and the sling represented the force which caused the pebble to apply the second law and change its direction.

Again, the fact of gravitation was known long before Newton studied it. Many an object must have fallen upon a philosopher's head before Newton was aroused by his mythical apple, and we have experiments by Galileo that showed a pretty clear notion of the law of gravitation as regards terrestrial objects. That all objects are attracted equally to the earth cannot be shown unless we remove obstructions from

their path. The buoyancy of the air will affect light masses more than dense ones; if the air be removed all substances will fall to earth with equal rapidity. Newton's great step was the extension of the idea of gravitation to celestial objects; and he claimed that all masses attract each other at all times, but that distance influences the intensity of this attraction.

By means of Newton's generalization astronomers have been able to calculate the mutual attraction of the various planets for each other and for the sun. The more closely celestial bodies approach one another, the more they affect each other's motions; with the help of Newton's law these irregularities in the orbits have been explained. The matter has been carried even further; from such perturbations of Saturn, Leverrier was able to predict the existence of the then unknown planet Neptune, and to tell owners of better telescopes than he possessed where to look for it.

Again, Newton was the first to explain the tides, and to show how they were due to the action of the moon and the sun upon the ocean, although the larger body, the sun, is so much farther from the earth than is the moon that its attraction is less apparent. The moon appears to revolve around the earth once in about twenty-four and one half hours, whereas the average interval between the successive appearances of the sun is twenty-four hours. The solar tide and lunar tide therefore pursue unequal rates. On the occasions when they come together we have the high or spring tides. When they oppose each other we have the low or neap tides.

More practical still were Newton's discoveries in optics. Telescopes had been made by Galileo and others before him, but the lenses employed were imperfect owing to the difficulties in the manufacture of glass, and the light in passing through them showed queer colorations. The images were blurred and surrounded by colored fringes. It is only

in recent days that all these imperfections have been corrected, and we now have glass lenses of forty inches' diameter, as in the great Chicago telescope. But Newton invented a telescope which was quite independent of glasses, using the principle which you can discover for yourselves by looking into the bowl of an ordinary tablespoon. The reflecting telescope has been much used, and the highest point reached in its construction was Lord Rosse's instrument, which was fifty feet long, six feet in diameter, and possessed a mirror weighing six tons.

Yet another practical device comes even more closely home to us. Navigators are indebted to Newton for the instrument next in importance to the compass, — the sextant.

The chromatic errors of lenses led Newton to study the nature of light so profoundly that he not only avoided the errors of his predecessors but also profited by them. Allowing a beam of sunlight to pass through the round hole of a shutter and fall upon a prism, he found that it was broken up, and that in place of a single white dot it became a streak of various colors. From this he inferred that white light is not simple but consists of various rays that can be separated by a prism. He attempted to recompose the light out of the colors into which he had dissociated it, and found here again that he was successful. From this discovery of Newton's there have been distinct advances in later times. It is found better to replace the round hole in the shutter by a slit. We then find that white light is decomposed to give a band of purer colors than that obtained through a round opening. It is called a spectrum, and is well known to most of you. This band can be shown to be made of little images of the slit placed side by side. Afterwards Fraunhofer showed that if the slit was made narrow enough, a large number of fine lines appeared across the spectrum. And later still, Bunsen and

Kirchhoff showed, first, that each chemical element emits certain rays having fixed places in the spectrum, and secondly, that many elements emit rays that coincide in their position with the lines discovered by Fraunhofer in the solar spectrum. From these coincidences we are enabled to assert positive knowledge as to the chemical constitution of the sun and other heavenly bodies far beyond the reach of any other known method of analysis.

Thus Newton seems by his magic touch to have opened doors to mysterious chambers in nature's mansion, some destined to become workshops for man's practical needs, some treasures of his mental wealth. Well did he deserve the eulogy of the poet Pope: —

“Nature and nature's laws lay hid in night,  
God said, ‘Let Newton be,’ and all was light!”

## OLIVER WOLCOTT GIBBS<sup>1</sup>

WHEN Oliver Wolcott Gibbs died, on December 9th, 1908, American chemists were bereft of one of their leaders, to whom they could look, with affectionate respect, as a pioneer in research, and the true example of the tireless seeker after truth, withal an earnest patriot and a noble gentleman. He was never at the head of a great university laboratory, and the last twenty-five years of his life were spent in retirement from all academic duties; no great body of students is left to mourn the loss of their former teacher. He wrote comparatively few papers of general interest and no books; he shrank instinctively from appearing in the public eye, and the idea of making even an informal after-dinner speech was hateful to him. His austere demeanor and dignified reserve must have always prevented his gaining popularity with the masses, even if his tastes had not led him to prefer scholarly seclusion. To what, then, shall we ascribe the influence which he wielded in the world of chemistry, so that foreign as well as American institutions of learning delighted in showering honors upon him, and considered themselves fortunate if they could obtain his coöperation and advice? Was it not because we all realized that this was a true High-Priest of knowledge, a guardian of the sanctuary, rather than an exploiter of its mysteries; one who could read without an accusing pang, that beautiful distich in which Schiller says of Science:—

“Einem ist sie die hohe, die himmlische Göttin, dem Andern  
Eine tüchtige Kuh, die ihn mit Butter versorgt.”

<sup>1</sup> Reprinted from *Proceedings, Am. Chem. Soc.* (1910), p. 69.

Gibbs, a man of modest wants, was probably always possessed of such means that he could restrict himself to the academic side of his profession, and his family traditions and early training would hardly have fitted him for business. I remember conversations with him about the successful careers of his friends, A. W. Hofmann and Joseph Wharton, which made it clear that he would not have attacked a technical problem with any degree of confidence. Perhaps, therefore, a knowledge of his own limitations may have assisted his natural predilections in determining the direction of his work toward pure, one may almost say abstruse, science. But his contemporaries saw a man seeking truth for truth's sake, and they put their trust in his disinterestedness, as well as in his scientific acumen and experimental skill. Justly conscious of his own worth, he was quick to recognize what was meritorious in the work of others, and to applaud, without reserve, the advances along lines quite foreign to his own point of view, while maintaining an almost pathetic veneration for his own great masters, between whom and the present generation he remained one of the last links. Cant, religious, moral or scientific, was abhorrent to him, and he could be cruelly caustic in his denunciation of what he deemed charlatanry or insincerity. On the other hand, where he once placed his trust, he left it implicitly, and, when his advice and help were sought, in good faith, he gave of his best. In appearance, and in some respect manners, he resembled James Russell Lowell, to whom I believe he was distantly related. It would have taken considerable boldness to be flippant in his presence, and his students, at all periods of his life, seem to have stood in great awe of him. But he was dearly beloved by friends in and out of academic circles, and he seemed to have the power of impressing his own enthusiasm upon those with whom he collaborated for the public good, as well as for the

advancement of science. The Union League and Century Clubs, of New York City, owe their foundation largely to his efforts, just as did the National Academy of Science in Washington; his effectiveness as a member of the U. S. Sanitary Commission, during the Civil War, seemed to have exacted the lifelong respect of all his associates.

While, therefore, it was an inestimable gain to the Lawrence Scientific School to secure this master of research, one cannot help wondering whether the narrowness which kept him out of his own alma mater, and forced him to leave the city of his birth, did not curtail some of his most useful powers. Furthermore, the policy which subsequent events have proved thoroughly mistaken, of reducing the Lawrence Scientific School in 1871 from its status as virtually a graduate faculty of natural and exact science, to a shadowy existence as an appendage of Harvard College, deprived Professor Gibbs of his teaching laboratory, and barred American students of chemistry from working under the direction of a guide who remained for another quarter of a century the master of inorganic research. In fact, during less than eight years of his entire career was he in a position to assign topics for independent research to students in his laboratory, and thus carry out those parallel tests which are the great resource of the modern university professor. Thus it is that the figure of Wolcott Gibbs, even though so recently faded from our eyes, towers in our memory like that of one of the early frontiersmen blazing out new paths in a primeval forest; like the heroes of James Fenimore Cooper, who seek the wilderness from love of nature, not from hatred of man, and who are solitary, not from a saturnine disposition, but from lack of followers willing to forsake easy harvest for the chances of a laborious chase.

But to those who were his immediate contemporaries,

Gibbs could not have appeared as a recluse. In the "American Journal of Science," he was for twenty-two years the eloquent interpreter of the trend of chemistry to workers in other fields of science, and, similarly, the early volumes of the "Berichte der deutschen chemischen Gesellschaft" contain his concise but adequate reports of the achievements of American chemistry. His understanding and sympathy for other branches of exact sciences was great, and, in fact, thermodynamics and optics received much of his attention: he it was who first appreciated the work of his namesake, J. Willard Gibbs, and insisted on the award of the Rumford Medal for that treatise on "Equilibrium in Heterogeneous Systems," which became famous twenty years later, when Le Chatelier rediscovered it for the benefit of modern chemists. I could instance, from personal observation, other judgments rendered by him on scientific matters of less moment, in which the clearness of his vision and the thoroughness of his examination proved that no accidental circumstances led him thus to anticipate the trend of physical thought. His contemporaries were stimulated both by the ideas which he freely placed at their disposal, and by the appreciative discrimination which he exercised toward their own scientific efforts.

Born in New York City, on February 21, 1821, as the second son of Colonel George and of Laura Gibbs, he was named after his maternal grandfather, Oliver Wolcott, Secretary of the Treasury under Washington and Adams. His boyhood was chiefly spent on his father's farm at Newtown (near what is now Astoria), Long Island, and he was educated at the Columbia Grammar School and Columbia College, from which he received the degrees of A.B. in 1841 and A.M. in 1844. He also graduated in medicine from the College of Physicians and Surgeons in 1845, though he never practiced

as a physician. His taste for physics and chemistry developed early; he published one or two papers as an undergraduate, worked with Dr. Robert Hare in Philadelphia in 1842, and went abroad in 1845 to specialize in chemistry, under Rammelsberg and Heinrich Rose in Berlin, and under Laurent, Dumas, and Regnault in Paris. Returning in 1848, he lectured at Delaware College and the College of Physicians and Surgeons, and was appointed Professor of Physics and Chemistry at the Free Academy of New York City, now the College of the City of New York, but then practically of high school grade. Here he taught, chiefly by lectures and recitations, until 1863, when he was called to Harvard to fill the Rumford Professorship on the Application of Science to the Useful Arts, then recently vacated by Eben Horsford. Attached to this professorship was the Chemical Laboratory of the Lawrence Scientific School, but this was consolidated with the College Laboratory in 1871, under Professor J. P. Cooke, and Professor Gibbs thereafter limited himself to courses in Physical Chemistry, continuing his chemical investigations with the aid of paid assistants.

In 1887, he was made Professor Emeritus, and retired to Newport, Rhode Island, where he had always spent his summers on property long in the possession of his family. Here he built a small laboratory, overlooking the beach, in which he continued to work for another decade, until his waning strength warned him to desist. He had lost his dearly loved wife, Josephine Mauran, shortly before his retirement from Cambridge, and he lived very quietly at Newport, attended by a devoted niece, interesting himself chiefly in horticulture as a pastime. He had little taste for the fine arts, but was passionately fond of nature and a friend of all living things. I vividly remember his indignation, one day, when, in the course of a walk, we came across a contractor who was pre-

paring to lop off from a beautiful old tree a great branch that extended into a street through which he wished to move the villa of a summer resident. When the man refused to listen to remonstrances, I was left to guard the tree, while the Doctor set off to find a policeman and finally routed out the Mayor of Newport, with the result that the house had a quarter mile more to travel and the tree was saved.

I have already stated that Gibbs's opportunity to teach advanced chemistry to students was limited to eight years: Professor F. W. Clarke has given an authoritative account of his teaching at this period, in his beautiful lecture before the Chemical Society of London.<sup>1</sup> My own experience came later, when I fortunately joined the very small class which attended the course in Chemical Physics to which he confined himself after 1871. The formal part of the lesson was frequently dismissed in a few minutes, in which he handed out his full lecture notes, to be copied at home: the remainder of the hour was devoted to experimentation or to purely informal discussion of problems arising out of the general topic. I do not think that the subject was ever treated exhaustively, but we all felt enriched and stimulated when the hour was over. Unfortunately, the course was not correlated to any other work in the University, and I doubt whether, at any one time, more than a dozen undergraduates knew Professor Gibbs by sight.

Privileged, half a dozen years later, to assist him at his private research laboratory, in Newport, I was able to observe more closely his methods of thought and work. He belonged emphatically to what might be termed the Berzelius type of chemist, basing his views upon an intimate knowledge of the reactions of a selected number of elements, and preferring direct deduction from qualitative or quantitative evidence

<sup>1</sup> *Journ. Chem. Soc. Trans.* **95**, 1299 (1909).

to the experimental substantiation of a hypothesis reached by inductive speculation. His synthetic researches were chiefly carried out in test tubes, without overexact measurements of reacting quantities, of temperature or other conditions. The elaborate search for an *optimum* production of a given compound, so familiar in recent inorganic work, did not appeal to him, and he frequently emphasized his desire to point out the directions in which complex compounds should be sought, leaving their careful study to others. Working with the simplest apparatus, almost exclusively in aqueous solutions, he certainly produced an astonishing number of new compounds, whose correlations he was able to point out with considerable verisimilitude. Perhaps he missed a reaction here and there; but few of his critics have been able to state that they failed to find what he did, when they followed his directions closely. As an analyst, he enriched us with some elegant methods, which are not sufficiently emphasized in textbooks: the determination of manganese as pyrophosphate; the use of mercuric oxide instead of a fixed alkali in precipitating various acids with mercuric nitrate; improvements in the estimation of bases as sulphates and oxalates; the detection of cerium by means of bismuth tetroxide or lead peroxide; the use of luteocobalt salts to characterize various acids. The determination of metals by electrolysis, the operation of difficult fusions downward instead of upward, the use of a comparison tube in eudiometric measurements, were all methods first published by him, and many methods developed by others were due to his suggestions. In physics, he early remedied defects in some types of galvanic cell, now obsolete, and he devised improvements of considerable value in the prism spectroscope.

A curious departure from his customary work was his reversion, late in life, to physiological chemistry, when he

undertook in 1889 with H. A. Hare and later with E. T. Reichert the systematic study of the action of definitely related organic compounds upon animals. His ideal was the establishment of principles whereby the physiological effect of drugs might be enhanced or modified step by step, so as to produce gradations of physiological effect comparable to the shading of the spectral colors. The experimental work was done by his associates, and did not progress far enough to lead to definite conclusions upon this idea.

The name of Gibbs will, however, be chiefly associated with his three great researches on the cobalt-ammines, the platinum metals and the complex acids. The oxidation of cobalt in ammoniacal solutions had been observed by Gmelin as early as 1822; but F. A. Genth first produced well-defined salts of an ammonia-cobalt base in 1847, publishing his results in 1851, in which latter year papers were published in France by Claudet and by Frémy, who defined four distinct series. Gibbs discovered xanthocobalt in 1852, and thereupon associated himself with Professor Genth, then at the University of Pennsylvania, in a thoroughly systematic study, to which Gibbs seems to have contributed the greater portion of the experimental detail. The results were published by the Smithsonian Institution in December, 1856; but the second series of the work was presented by Gibbs alone to the American Academy of Arts and Sciences in 1874 and 1875. These papers are noteworthy for the thoroughness with which each of the many series was studied, analytically as well as synthetically; he not only showed that the same type of cobalt-ammine could persist through various combinations with different acids, but also proved that certain acid groups, like  $\text{NO}_2$ , must be frequently considered an integral part of the base, and that this was notably true of the water, considered by others mere crystal-water, which distinguished the

composition of the roseo- from the purpureo-cobalts. His researches were the natural foundation of Werner's theory, which has gained general recognition during the past fifteen years.

Analogy to cobalt-ammines appeared to exist in a compound obtained by Frémy in 1844, by the action of ammonium chloride upon potassium osmiate, and Gibbs proved this, in a brief note published with Genth in 1857, by showing that chlorine could be replaced by other negative radicals without altering the Os : NH<sub>3</sub> ratio. In his final paper, in 1881, he named these compounds the osmyl-tetrammine series. But he was deflected from the continued study of the ammines of the platinum group, which he had evidently proposed to himself in 1858, by the interest which the separation and complete characterization of these metals themselves had excited. Working chiefly with refractory California ores, he found it necessary to develop new methods of attack, and his work may well be placed by the side of that of Claus and St. Clair-Deville.

Meanwhile, the platino-ammines were fully studied by other observers, and Gibbs rather devoted his attention to the behavior of the platinum group to acids. In 1877 he found that the oxides of these metals would unite with the tungstates, to form the salts of complex acids, analogous to the silico-tungstates of Marignac, and this was the starting-point for his great researches on the complex acids, which virtually monopolized the remainder of his experimental activity. Beginning with attempts at systematizing the straggling data on silico-tungstates, phospho-tungstates, etc., recorded by other observers, through the preparation of parallel compounds, he was led to draw one element after another into the complicated molecules that gather around the tungstic or molybdic nucleus. With a large corps of assistants at his disposal, the

work would have assumed gigantic dimensions; but, with a single assistant to carry out the most subtle quantitative separations, his theories must, perforce, await mathematical confirmation, and his cabinet must contain scores of unanalyzed compounds. I believe that he regarded the tungstic acids more or less as the inorganic analogues of hydrocarbons, with certain typical arrangements, into which other groups could enter by direct substitution, largely merging their own identity. Probably, the majority of modern investigators ascribe a more important rôle to these elements of lesser atomic mass; but viewed from the standpoint which I have indicated, the work of Gibbs will show a remarkable consistency, just as his experimental data will, undoubtedly, be confirmed in all essentials by the work of his successors.

And thus the American Chemical Society may well inscribe among its immortals the name of an honorary member, with the words of one of his favorite authors: —

“Wer es den Besten seiner Zeit hat gleich gethan  
Der hat gelebt für alle Zeiten.”

## THE CHEMISTS' CLUB, NEW YORK<sup>1</sup>

THE Club occupies the lower portion of the new Chemists' Building, at 50-54 East 41st Street, completed in March, 1911. This building occupies a lot 56 feet by 100 feet, in the immediate vicinity of the Public Library and the Grand Central Station. It is owned by a stock company whose shareholders are chemists, manufacturers and companies employing chemical processes, and it is to be conducted for the furtherance of chemical industry and research: in certain eventualities, The Chemists' Club can acquire ownership of the building.<sup>2</sup> The five uppermost stories — not controlled by the Club — are constructed for chemical laboratories.

The Club's quarters may be described as follows: The vestibule opens into a large oak-paneled entrance-hall, one side of which serves as an office, the other as a lounging-room; a wide corridor leads thence to the main stairway and to the auditorium, which occupies the entire rear half of the lot. This auditorium seats 300 persons and has a lecture platform completely equipped for scientific demonstrations: it is decorated in classic style, and is a very lofty and well-proportioned room.

The upper floors of the Club House are reached by a very beautiful stairway, quite independent of the public stairway and elevators. The first landing leads to the auditorium balcony and also to the lavatories. Then comes the first, or social, floor, the front half of which, a mahogany room 52 by 23 feet, is furnished for general social purposes; in the rear is the

<sup>1</sup> Reprinted from the Year Book of the Club for 1910-11.

<sup>2</sup> Dr. Loeb himself was the largest shareholder, and in his will left his holdings to the Chemists' Building Company for cancellation, thus very materially reducing the amount of stock to be acquired by the Club. [EDITOR.]



THE CHEMISTS' BUILDING,  
52 EAST FORTY-FIRST STREET, NEW YORK



restaurant, with a roof-garden for summer use. The adjacent spacious pantry is connected by dumb-waiters with the kitchen and supply-rooms that are situated in the basement. For Club banquets the entire floor-space is available. The second story is known as the Scientific Floor: it is exceptionally lofty, to accommodate a gallery in the Library, which has the same dimensions as the social room, immediately below, and whose shelves can hold upwards of 16,000 volumes, with additional space in reserve. This room is named Chandler Hall, after the first president of the Club, and it will prove an ideal work-room for the scientific student. The rear half of this floor is to be used as a scientific museum, according to a plan devised by a committee of the American Chemical Society, but not yet fully developed. Out of it there opens the board-room, which, in conformity to the character of the museum, has been designed in imitation of an alchemist's laboratory and adapted to the preservation of specimens of old chemical apparatus. A small photographic dark-room and storage for unbound pamphlets are likewise to be found on this floor.

The fourth and fifth stories are residential, and provided with rooms for either transient or permanent occupancy. There are two suites, consisting of sitting-room, bedroom and bath-room, with a private corridor, and eighteen other bedrooms, a number of which are provided with private bath-rooms. Each suite or room is named after a college or university, whose alumni have furnished it, and this serves to accentuate the academic spirit of the Club membership. The institutions thus commemorated are: Harvard, Yale, Princeton, Columbia, Pennsylvania, New York University, Massachusetts Institute of Technology, German Universities, Cornell, British Schools and Universities, Johns Hopkins, University of Virginia, University of Michigan, The College

of the City of New York, Imperial University of Japan, Swiss Universities, Western Universities.

All the floors are connected by telephone with the central switch-board on the entrance floor, and the same board serves the tenants of the laboratories in the upper stories.

It is also interesting to note that the Club controls three small laboratories, named in memory of Wolcott Gibbs, Robert Bunsen and August W. v. Hofmann, which are equipped for the transient use of Club members.<sup>1</sup> Applications for their use must be made at the Club office.

<sup>1</sup> To these the Chemists' Club has added a fourth memorial, consisting of the two rooms which constituted Dr. Loeb's laboratory. This is known as the Morris Loeb Laboratory.

[EDITOR.]

## THE CHEMISTS' BUILDING<sup>1</sup>

THE opening of the new Chemists' Building in New York City is an event of national, rather than merely local significance, and the committee in charge has done its duty by seeking to express this fact in the programme of the opening exercises. The social comforts of The Chemists' Club are but an incident in the general scheme, and, in fact, the physical transfer of that organization from its present quarters to the splendid home now provided for it must, necessarily, await the completion of its furnishings, after the building itself was declared ready for occupancy. Hence, the Club's festivities were subordinated to the dedication ceremonies of the building, when due emphasis could be laid upon the serious aims of the enterprise, and to the scientific meetings, under the auspices of the local sections of our Society, the American Electrochemical Society and the Society of Chemical Industry. It will not be the fault of the speakers at these meetings, if the general public fails to grasp the importance of chemistry in our industrial development, and also as a branch of pure science. We ourselves, and, especially, those of us who do not dwell in New York itself, or its immediate vicinity, might well take this occasion to reflect upon the practical significance of this undertaking.

Nobody can review the history of American progress during the past twenty-five years without recognizing how much more intimately chemistry is enmeshed in the general economic and sociological texture than a quarter century ago. Then, the American student who went beyond the general chemical courses prescribed for all freshmen and sopho-

<sup>1</sup> Editorial, reprinted from *Journ. Ind. and Eng. Chem.*, **3**, 205 (1911).

mores did so as a preparation for medicine or some other recognized profession, or with the definite purpose of entering an academic career. The possibility of establishing himself as an independent chemical analyst or expert was certainly never placed before the student; and the works-chemist, in the eyes of the industrial world, was held in the sort of regard which may be likened to Lincoln's estimate of the value of brigadier-generals, when he remarked, on hearing that a Confederate raider had cut out a baggage train and captured three generals, "I can make a brigadier any day, but mules cost money." Under such conditions, chemistry as a profession could have slight standing, and the gregarious needs of its votaries were amply met by the annual "meetings" of Section C of the American Association for the Advancement of Science, and by occasional local gatherings. The reorganization of the American Chemical Society on a national basis, in June, 1890, presaged the change which seems to have followed the World's Fair at Chicago. We need not inquire too closely whether the lean years following the financial crisis of 1893 caused manufacturers to appreciate more fully the value of chemical control of their processes, or whether the exhibits of German and other foreign manufacturers, coupled with the demonstration of the World's Chemical Congress, attracted the attention of the American public to the possibilities of the development of a true chemical industry. Whatever share these or other influences may have borne, the result may be strikingly shown in a circumstance connected with the opening ceremonies of the Chemists' Building. In the preface to Volume XII of the "Journal of the American Chemical Society," the editor estimated the number of chemists *available* for the newly-formed New York Section at two hundred; twenty-one years later, with duplicates eliminated, thirteen hundred invitations were sent out

to the *enrolled* members of the New York local sections of the three large chemical societies.

Of course, in this phenomenal development of the chemical profession, America is merely catching up with European progress, not leading it. The enormous attendance at the recent Triennial Congress of Applied Chemistry was well calculated to astonish the non-chemical world; and if the initiative taken at Chicago in 1893 toward convening these congresses is to our credit, the contrast between the two hundred and fifty men then in attendance and the chemists who will crowd New York in October, 1912, will convince America not only that progress has been made, but also that still greater advances must be accomplished here, to keep pace with chemical industry abroad. The American Chemical Society would not fulfil its duty toward its membership by holding occasional meetings and publishing the proceedings thereof; it must afford them a means for the prompt publication of their researches, as well as for their information upon the world's progress in pure as well as applied science; its journals must be the link which binds the isolated worker to his profession. But there are still other needs; the relations of the professional chemist toward the industries must be established on a sounder basis; the elimination of wasteful methods of manufacture through chemical control must be advocated more forcibly and pervasively; chemical industry must coöperate more closely toward the furthering of mutual interests, toward the establishment of more satisfactory manufacturing conditions, from the legal, as well as from the hygienic and economic aspect; aids must be devised for the furtherance of research, along industrial as well as purely scientific lines.

All of these ideas have been expressed at one time or another by the promoters of the American Chemical Society, and they were also in the minds of the founders of The Chemists' Club

of New York, which for the past twelve years has maintained, at considerable pecuniary sacrifice on the part of its members, an organization in which the social features were infinitesimal as compared with the furtherance of the above-named objects. The new Chemists' Building represents the concrete embodiment of these ideals, and the participants in the Eighth International Congress will find established in New York City the first building devoted to the furtherance of chemical science and industry by *all* those means which are not distinctly pedagogical. This is a somewhat bold assertion, but it will bear analysis.

It is needless to descant upon the advantages to be derived from a well-equipped social club, which affords an attractive gathering-point for the local chemist, as well as housing accommodations for the non-resident member. But it might be well to bear in mind that the industrial chemist usually visits New York for professional consultation, or for the discussion of important business propositions; the technical library is an indispensable tool which he can now employ without quitting his shelter. Indeed, if a problem arises suddenly that requires experimental test, the laboratory in which to try it can be obtained with no more formality than that needed for engaging a bedroom. For quite a number of years, The Chemists' Club has made it an object to promote the interests of young chemists, as well as those of the manufacturer, by maintaining a professional employment bureau, which was chiefly hampered by the lack of a permanent office. Could this not be established in the new Club-house in such a manner as greatly to facilitate the establishment of communication between the dispenser and seeker of employment?

The existence of a complete building, devoted solely to the interests of the chemists, will probably be the best demon-

stration to the American public of the importance which this profession has now assumed from the technical standpoint. The consulting chemist, housed in laboratories for his own use, can well expect greater consideration than the man who is obliged to conduct his work in a ramshackle rookery, or, at best, in an out-of-the-way corner of a general commercial building. But, apart from any mere question of ostentation, the business man or manufacturer frequently fails to seek chemical advice, on questions of real importance, from ignorance of the manner of setting about it and sheer indolence in ascertaining it. Many do not even seem to know that there is such a man as a consulting chemist. May not some eyes be opened and some extravagant waste of natural resources be avoided, by persistent efforts of the manager of this central home of chemistry, and the rule of thumb be replaced by the rule of scales?

The American Chemical Society has gradually accumulated a library of considerable magnitude, which has been deposited of recent years with The Chemists' Club, which organization has acquired, by gift and purchase, many volumes of its own. But the shelf-space has been so limited, that but few of the books were accessible and even then could only be consulted under unfavorable conditions. In the magnificent "Chandler Hall" the entire library will be available for consultation at all reasonable hours. It is also planned to establish a collection of duplicates, to be loaned freely to reputable chemists throughout the country. Here again, the provision of a suitable working-place will serve not merely the local interests, but, perhaps even more effectively, the scattered outposts of chemical endeavor.

One of the chief disadvantages under which the American investigator labors is the difficulty of obtaining research material. The German or French experimenter can obtain,

within twenty-four hours, a specimen of virtually every chemical substance that is in the market: the American depends upon the stock of two or three importers, which must necessarily be limited in regard to the rarer preparations, or he must import directly, with inevitable delays in transit and especially at the custom-house. The Chemical Museum is planned to obviate this, by keeping as complete a collection of substances as possible, in relatively small quantities, it is true, which will be loaned to investigators who require material for preliminary investigation. Such a preliminary test may go far towards determining the course of a research and deciding whether it is worth the chemist's while to procure larger quantities. But, the projectors also hope to induce the American chemists to deposit with the Museum samples of all new substances prepared in their researches, to serve a similar purpose as do type specimens in a museum of natural history as standards of comparison for future investigators. Here we should have the first chance of facilitating chemical research in America by coöperation, instead of by subsidizing individual investigations. It will take some time to perfect the plans; but if it can be accomplished, the student in a Rocky Mountain college will be within as easy reach of his materials as his fellow in a large city of the East.

We have detailed some of the more striking advantages which the new building is expected to confer upon the chemical profession as a whole, as well as upon its individual votaries; is it an exaggeration to characterize the constitution of the Chemists' Building Company itself as a new era in the chemical industry of our country? In scanning the list of shareholders, we find representatives of nearly every important concern, or even the larger companies themselves; but that this is not a "trust," in the sense so obnoxious to the yellow journalist, is demonstrated by the conditions of the

partnership. No shareholder can receive more than 3 per cent dividends, and the surplus cannot, under any circumstances, accrue to his benefit within the next fifty years. This association, therefore, is not for individual profit, but for the *raising of the standards of chemical industry and research in the United States*. If we recognize what the Verein zur Hebung der chemischen Industrie, founded by Hofmann and Werner Siemens, has done for Germany, we may well hope for further fruits of this initiative here. Perhaps this building will house joint laboratories for the solution of questions affecting all manufactures alike; or experimental stations for the study of natural products not yet utilized; or a coöperative bureau of standardization for analytical methods; or a national welfare bureau for employees in chemical factories. This building does not owe its erection to some benevolent demigod, extending his protecting wing over people unable to care for themselves; it is a building by the chemists, of the chemists, and for the chemists. May it ever serve as an exemplar of unselfish patriotic coöperation!

## ADDRESS

AS PRESIDENT OF THE CHEMISTS' BUILDING COMPANY  
ON THE OCCASION OF THE OPENING OF THE CHEM-  
ISTS' BUILDING, MARCH 17, 1911<sup>1</sup>

I RISE to welcome you on behalf of the directors and stock-holders of the Chemists' Building Company, and to thank you for the interest which your presence indicates in the formal opening of a building which we believe to be the first of its kind, not only in this country, but on earth. It is true that Berlin possesses in the Hofmann-Haus a home for the German Chemical Society and that London owes to the munificence of the late Ludwig Mond its Davy-Faraday Laboratories for Chemical and Physical Research. But this new building in which you find yourselves is planned to serve under one roof the social, intellectual and practical needs of the chemical profession not of New York alone, but of our whole beloved country.

The means for its construction have been furnished by men, many of whom can expect to share to but a slight degree in the benefits of The Chemists' Club, which occupies so much of its floor space. These shareholders see in it the incarnation of some of the ideals that led them to the pursuit of chemistry, pure or applied, as their lifework.

For, strange as it may seem to the layman, who has seen the ugliest blots on a landscape designated as chemical factories, who has sniffed with disgust a chemical odor, has been urged to believe that the chemist's shadow contaminates pure foods, and has been taught in school that alchemy spelled fraud and sorcery, our science is one calculated to

<sup>1</sup> Reprinted from *Met. and Chem. Engineering*, 9, 177 (1911).

develop the ideal side of human nature, and the chemist, more perhaps than the votary of natural science or the devotee of the so-called humanities, is led to an intense interest in human development.

Our science aspires not only to know, but also to do. On the one hand, it leads us to delve into the secrets of nature, in the minute atom as well as in the far distant stars, in the living cell as well as in the crystallized relics of the convulsions from which this earth was born; on the other, it leads us to apply this knowledge to the immediate needs of man, be it in safeguarding his health, in ministering to his material or esthetic wants, or in regulating his commerce and in facilitating his utilization of the earth's resources. These many points of contact with nature and with human interest will be the theme of the eminent men whom I shall have the privilege of introducing this afternoon and will be illustrated at greater length in the scientific meetings which are to follow; it is enough that we recognize at this moment that this versatility of method and of purpose must necessarily enlarge the viewpoint of the chemist, and that we seek therein the motives for the ready coöperation in the present enterprise.

Our shareholders content themselves with a moderate return for their money and have agreed that any surplus profits shall accrue to the benefit of chemical science. They hope that the facilities afforded within these walls will redound to the benefit of mankind and the prosperity of the country.

May I emphasize the word "facilities"? There are two ways of aiding a man or a cause: by addition to the income or reduction of the expense. The pecuniary result to the beneficiary may be the same, but the moral one is far different; it is not only the beggar who is pauperized by the cash gift and uplifted by the aid which enables him to earn his own livelihood. Arts and sciences may be stimulated by prizes and

scholarships beyond a doubt, but the relation between donor and recipient is not free from restraint, and the probability of human error in the selection of the right incumbent makes the method a wasteful one at best.

Far better is it to remove those obstacles which hamper all work equally and are felt more severely by those whose means are restricted and who have not yet earned the recognition of the world at large. The laboratory student is encumbered by certain restrictions in America more than elsewhere. The higher price of commodities affects him in many ways besides the higher cost of living, rent of laboratory, installation of equipment, purchase of supplies, salary of assistant, acquisition of books. The advanced cost of labor militates against the construction of certain grades of apparatus and the preparation of the rarer chemicals in this country; and a curiously unscientific tariff law, while pretending to lift the duty from articles required for educational purposes, practically forces the colleges to make their purchases abroad and prevents American dealers from carrying an adequate selection of imported material. It is no exaggeration to state that this duty-free importation clause, as interpreted by the United States Treasury Department, forces the American chemist to wait from two to three months before making an experiment for which he could obtain his material in two or three days if he were working abroad..

To remove these disadvantages in time and cost, to provide easy access to books and apparatus, to make room for the independent scientific worker, are the ideals which hovered before the eyes of those who planned this present enterprise. Time will show whether they can all be realized, but whatever is done in this beautiful building, which we are about to dedicate, must open free opportunities to all and show favoritism toward none, if the trust imposed upon its management

be administered in the spirit of those who have contributed toward its erection.

A library of the highest scientific importance and a museum of chemical substances will be available for every reputable chemist; laboratories for temporary as well as for permanent use will be at the disposal of the earnest student; help and advice will be extended to the struggling beginner; good comradeship and hearty coöperation will characterize The Chemists' Club, and this auditorium, soon to be named after the first great chemist of American birth, will ever minister to his ideal of the application of science to the useful arts.

## THE COAL-TAR COLORS<sup>1</sup>

THE term "coal-tar colors" is applied to coloring matters artificially prepared from coal-tar, chiefly from the hydrocarbons extracted from it.

The first observation of a colored compound of this class was made by Runge in 1834; but the real beginning of the great modern color industry dates from 1856, when W. H. Perkin obtained a violet dyestuff by oxidizing impure aniline with chromic acid, took out a patent for it, and commenced manufacturing it in England. Many other dyes were subsequently obtained from aniline and the substances related to it, by A. W. Hofmann, Griess, Girard, Lauth, and many others. But the most sensational step was the preparation by Graebe and Liebermann (1868) of a natural dyestuff — viz., the coloring principle of madder-root — from the anthracene of coal-tar. In 1880 indigo was first prepared, not from coal-tar products, but by a purely synthetic method, and other natural colors have since been prepared in a similar manner; so that natural dyestuffs reproduced by artificial means need not necessarily originate from coal-tar. The artificial indigo and alizarin are not mere substitutes for the natural indigo and madder; they are chemically identical with them, and surpass them in purity, and their adaptability to special methods in dyeing and printing often makes them even more desirable. But as the cost of manufacture is high, they compete with the natural products on about equal terms.

The color industry was first developed in England and France, but the more thorough technical instruction at the

<sup>1</sup> Reprinted from the *New International Encyclopaedia* (Dodd, Mead & Co., New York, 1912, 5, 74-77), by permission of the Publishers.

German universities produced a body of skilled manufacturers and investigators who soon took the lead. At present, in addition to the great factories near Berlin, Frankfurt, Elberfeld, and Mannheim, and a host of smaller ones in various parts of Germany, German capital controls many of the establishments in France, Russia, and other countries. The United States possess few independent factories, and the list of their products is rather limited; indeed, American dyers appear to call for a smaller range of dyestuffs than those of other countries. A peculiar development of the last fifteen years is the extension of the methods of the dye industry to the production of artificial drugs, such as antipyrin, antifebrin, etc., many of which are manufactured in the same establishments which control the dye patents.

**CLASSIFICATION.** Artificial colors were formerly classified merely according to the sources from which they were obtained. Thus, many of them, including magenta, "aniline blue," "aniline green," "aniline yellow," etc., were grouped together as *aniline colors*. At present somewhat different systems of classification are used by different authors, but all systems are based exclusively on the chemical constitution of the dyes.

Many attempts have been made to find a general answer to the question: What must be the chemical nature of a carbon compound in order that it may be a dye? An all-embracing answer to this question has not yet been found. But experience has shown that the true dyestuffs exhibit peculiar groupings of the constituent atoms. Such "chromophore" groupings produce, however, only a *tendency* toward color, but not necessarily colors; indeed, many compounds containing them are perfectly colorless, and the majority of true dyes become colorless if deprived of the small amount of oxygen they contain, although their chromophore groups

may not be in the least affected. If, however, a chromophore group is combined with certain other atomic groups, the result is a dye. For example, the so-called *azo-group* ( $-N=N-$ ) is chromophoric; the compound called azobenzene,  $C_6H_5-N=N-C_6H_5$ , although colored red and evidently containing the azo-group, is not a dye; but it becomes one when the so-called amido-group ( $NH_2$ ) also is introduced into its molecule, the compound  $C_6H_5-N=N-C_6H_4NH_2$ , called amido-azobenzene, being a true dye. If, instead of the amido-group, a hydroxyl group ( $OH$ ) is introduced, the result is again a dye (an orange one). Further, the tints of dyes are produced by variation in the "substituting" groups which replace hydrogen in the primitive molecule. Thus, the introduction of the methyl group ( $CH_3$ ) generally increases the violet tendency; the phenyl group ( $C_6H_5$ ) produces bluish tints; the naphthyl group ( $C_{10}H_7$ ) a tendency toward brown-red, etc. The relative position of the groups likewise plays a large part in the determination of color. But, as we have already observed, a definite and all-embracing rule does not exist. Frequently compounds must enter into combination with a base or an acid before they will fix themselves upon the fibre, and then the tints are frequently affected by the different bases or acids to a varying degree. For example, alizarin dyes red with the hydroxide of aluminum, and black with the hydroxide of iron.

For the purposes of the present sketch, the coal-tar colors may be grouped in five classes: viz., the azo-colors; triphenyl-carbinol derivatives; quinone derivatives; diphenyl-amine derivatives; and indigo dyes.

**Azo-COLORS.** The characteristic compound of this class is azo-benzene,  $C_6H_5N=NC_6H_5$ , already mentioned above. We have seen that the introduction of either  $NH_2$  or  $OH$  in place of a hydrogen atom produces a coloring matter—yellow

in the former, orange in the latter instance. Replacing either or both of the phenyl groups ( $C_6H_5$ ) by more complex hydrocarbon groups deepens the tone (with a tendency toward the redder tints), increases the affinity for fibres, and diminishes the liability to fade. The earlier dyes of this class, such as "aniline yellow," "Bismarck brown," chrysoidin, etc., were singularly brilliant, but were not fast; whereas the browns and the many reds, ranging from scarlet to purple, which are now produced under the names of ponceaux or bordeaux, congos, quinoline red, etc., are exceedingly permanent. In manufacturing this class of dyes, nitrous acid is allowed to act upon an ice-cold solution of the salt of any primary base (like aniline), and the "diazo-salt" formed is allowed to act on another base or a phenol; an endless variety of combinations is thus possible.

**TRIPHENYL-CARBINOL DERIVATIVES.** These represent the first discoveries in the aniline dyes, and some of them are still produced on the largest possible scale. The fundamental compound of the class is triphenyl-carbinol ( $C_6H_5)_3COH$ , and its derivatives are properly subdivided into *rosanilines*, *rosolic acids*, and *phthaleins*.

In the rosaniline group, two or three amido-groups ( $NH_2$ ) are introduced in place of hydrogen atoms of the phenyls ( $C_6H_5$ ). The *di*-amido-compounds are green; the *tri*-amido-compounds are red, violet, or blue. Strictly speaking, the compounds thus obtained are not themselves dyes, but are bases which must first be combined with suitable acids, and thus brought into a soluble form. Their salts in the solid condition are beautifully crystalline bodies, showing colors quite different from those of the solutions, and having peculiar lustres like those of beetles' wings. The solutions have very intense colorations and stain animal fibres readily and permanently, although they do not fix themselves easily

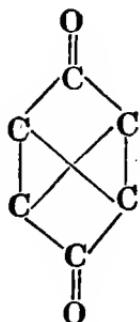
upon cotton or linen. They are the most brilliant and lively dyes, but are strongly affected by sunlight, and are consequently less useful than some dyes of other classes. They are generally manufactured by oxidizing processes at a comparatively high temperature, whereby two or three simpler compounds are welded, as it were, into compounds of complex molecular structure. Thus, in the manufacture of the well-known magenta dye (a tri-amido-compound) approximately equal quantities of aniline, ortho-toluidine, and para-toluidine are heated from 8 to 10 hours with arsenic oxide to  $190^{\circ}$  C., in large iron kettles. A very thick mass results, which can be extracted with hot water, and the compound thus obtained is found to be made up of molecular quantities of aniline, ortho-toluidine, and para-toluidine chemically combined.

Rosolic acid and its derivatives are made by the condensation of various phenols, three phenols being condensed into one compound of the rosolic acid group, just as the bases are condensed into one compound of the rosaniline group. The comparatively few dyes of this group give various shades of red. The hydroxyl groups, and hence the acid character of the phenols, remain unchanged in the products of condensation; the latter therefore combine with bases, and then they readily go into solution.

The phthaleins differ from the rosolic acids in so far as one of the three phenyls of the triphenyl-carbinol is connected in them with a carboxyl group ( $\text{COOH}$ ), the other two phenyls having one or more hydroxyls apiece, as in the rosolic acids. The phthaleins were discovered by Adolph von Baeyer, and are chiefly remarkable for the fluorescence of their alkali salts in solution. They are prepared by heating phenols with phthalic anhydride and a little sulphuric acid; when resorcin is taken as the phenol, a very well-known compound is obtained,

which has been called *fluorescein*, while its sodium salt is known as *uranin*. Solutions of the latter are yellow by transmitted light, but bright green by reflected light. This fluorescence is so intense that it is distinctly noticeable in extremely dilute solutions; so that this salt has been used to trace subterranean watercourses supposed to connect two neighboring bodies of water, the dye being thrown into one of these and fluorescence being subsequently noticed in the other. The potassium salt of a brominated fluorescein is *eosin*,  $C_{20}H_6O_5Br_4K_2$ , with a magnificent red and yellow fluorescence. These fluorescences disappear on the fibre, but eosin and analogous substances impart very brilliant flesh-tints to silk and wool.

**THE QUINONE DERIVATIVES.** These contain the characteristic nucleus —



and are almost invariably colored, although they become suitable for dyes only when they also contain several hydroxyl groups. By far the most important substance of this class is alizarin, which was already mentioned as identical with the active principle of madder. Anthracene, a coal-tar hydrocarbon, is converted into anthraquinone by heating with potassium bichromate and sulphuric acid; the anthraquinone is acted upon by fuming sulphuric acid, and

the resulting compound is melted with caustic soda, yielding a sodium salt of alizarin. This is soluble in water with a fine red color, but does not fasten upon any kind of fibre. If, however, cotton is previously impregnated with salts of aluminum, iron, or chromium, the alizarin will form insoluble salts ("lakes") with these metals; and as the precipitation occurs within the pores of the fibre, subsequent washing cannot remove it. Colors of this class of dyes are not suitable for silk and wool, but are very intense and permanent when properly applied to cotton.

**THE DIPHENYLAMINE DERIVATIVES.** These include many varieties of dyes, such as the indulins, indophenols, thiazins, etc. Their chemistry is too involved to be disposed of in a few words. It may, however, be mentioned that their characteristic groups are similar to anthraquinone, excepting that the oxygen of the latter is replaced by sulphur, imido-groups, etc. The more important dyes of this class include methylene blue and aniline black.

**INDIGO DYES.** By far the most important of these is indigo itself, a vegetable dye obtained from a tropical plant cultivated in India since the earliest times. The sap of this plant, when fermented under conditions excluding oxygen, yields *indigo white*, a soluble material having the formula  $C_{16}H_{12}N_2O_2$ ; if the fermentation proceeds in the open air, *indigo blue*,  $C_{16}H_{10}N_2O_2$ , is produced. This substance is a derivative of the base called indol,  $C_8H_7N$ , which occurs ready-formed, in small quantities, in many animal and vegetable secretions. It can be prepared artificially from aniline and chloraldehyde. When indigo was found to consist of two indol molecules joined together and oxidized, the clue for the production of artificial indigo was at hand. It has since been found that any benzene derivative having a nitrogenous group and a two-carbon group in the "ortho" position may give rise

to the formation of indigo. The first practical method, devised by Baeyer in 1880, involved the action of potassium hydroxide on ortho-nitropropionic acid; but many other methods have been devised since then, such as the action of melted potassium hydroxide on bromacetanilid, the action of halogenated acetone on aniline, etc. Indigo is one of the most reliable dye-stuffs, both as to brilliancy and permanency, and there is little difference in these respects between the natural and artificial products. The finished compound can, however, only be used after reduction to the soluble indigo-white, and this makes its use in dyeing and printing somewhat cumbersome. In some of the methods for preparing artificial indigo, the fibre can be impregnated with one ingredient and the other applied either in the dye-vat or from the printing-rolls; consequently, indigo can be and is often directly prepared in the quantities and in the places in which it is needed.

**LIST OF COLORS.** The following are some of the best known commercial coal-tar colors, their molecular formulas, and the principal methods employed in their manufacture.

*Analdehyde Green.* — See Aniline Green below.

*Aniline Black*,  $C_{30}H_{25}N_3$ , made by the oxidation of aniline with mineral salts.

*Aniline Blue* (triphenyl-rosaniline hydrochloride),  $C_{38}H_{35}N_3Cl$ , made by heating rosaniline, benzoic acid, and aniline, and subsequently adding hydrochloric acid.

*Aniline Brown*, Bismarck Brown, or Phenylene Brown (triimidoazobenzene),  $C_{12}H_{13}N_5$ , made by the action of nitrous acid on metaphenylene-diamine.

*Aniline Green*, or Aldehyde Green,  $C_{22}H_{27}N_3S_2O$ , made by the action of ordinary aldehyde on an acid solution of rosaniline sulphate and the subsequent addition of sodium hyposulphite.

*Aniline Orange.* — This name is applied to various compounds made by the action of amidosulphonic acids on phenols. The name is often applied to the so-called Victoria Orange,  $C_7H_6N_2O_5$ .

*Aniline Red.* — See Fuchsin below.

*Aniline Scarlet*,  $C_{18}H_{15}N_2O_4SNa$ , made by the action of diazoxyleno on naphthol-sulphonic acid.

*Aniline Violet.* — See Mauvein below.

*Aniline Yellow* (hydrochloride),  $C_{12}H_{12}N_3Cl$ , made by the action of nitrous acid on an excess of aniline.

*Alizarin*,  $C_{14}H_8O_4$ , made artificially by successive treatments of anthracene with chromic acid and fuming sulphuric acid, and melting the product with potassium hydroxide. Among the dyes allied to alizarin are: *Alizarin Black*,  $C_{10}H_6O_4.NaHSO_3$ ; *Alizarin Blue*,  $C_{17}H_9NO_4$ ; *Alizarin Orange*,  $C_{14}H_7NO_6$ ; and *Alizarin Violet*, or Gallein,  $C_{20}H_{10}O_7$ .

*Auramin* (hydrochloride),  $C_{17}H_{24}N_3OCl$ , made by the successive action of phosgene gas (carbon oxychloride) and ammonia upon dimethyl-aniline.

*Aurantia* (ammonium salt of hexanitro-diphenylamine),  $C_{12}H_6N_7O_{12}NH_4$ , made by the action of nitric acid on methyl-diphenylamine.

*Aurin*,  $C_{19}H_{14}O_3$ , made by the action of oxalic and sulphuric acids on phenol.

*Benzaldehyde Green*. — See Malachite Green below.

*Benzidine Red*. — See Congo Red below.

*Benzopurpurins*, dyes of various red shades. They are chemically allied to Congo Red (which see below), and are made by treating salts of toluidine (which is made from nitrotoluene, and is analogous to benzidine) with nitrous acid, and combining the resulting salts with  $\alpha$ - and  $\beta$ -naphthylamine-sulphonic acids.

*Bismarck Brown*. — See Aniline Brown above.

*Blackley Blue*. — See Indulin below.

*Bordeaux*. — See Ponceaux below.

*Chrysoidin* (hydrochloride),  $C_{12}H_{13}N_4Cl$ , made by the action of diazo-benzene chloride on metaphenylene-diamine in aqueous solution.

*Congo Red*, or Benzidine Red,  $C_{32}H_{22}N_6S_2O_6Na_2$ , made by the action of nitrous acid and then of sodium naphthionate on benzidine hydrochloride.

*Eosin*,  $C_{20}H_6O_5Br_4K_2$ , or  $C_{20}H_6O_5Br_4Na_2$ , made by the action of bromine on fluorescein.

*Erythrosin*,  $C_{20}H_6O_5I_4Na_2$ , made by the action of iodine on fluorescein.

*Fluorescein*,  $C_{20}H_{12}O_5$ , made by the action of phthalic acid anhydride on resorcin.

*Fuchsin*, Rosaniline Hydrochloride, Magenta or Aniline Red,  $C_{20}H_{20}N_3Cl$ , made by the oxidation of toluidine and aniline in the presence of acids.

*Gallein*. — See Alizarin above.

*Helianthin*. — See Methyl Orange below.

*Indigo*. — See text of the article above.

*Indulin*, or Blackley Blue,  $C_{18}H_{16}N_3$ , made by heating aniline salts with amidoazobenzene.

*Magenta*. — See Fuchsin above.

*Malachite Green*, Benzaldehyde Green, or Victoria Green,  $3C_{23}H_{26}N_2Cl.2ZnCl_2+H_2O$ , made by the condensation of benzaldehyde with dimethyl-aniline, and the subsequent addition of hydrochloric acid and zinc chloride.

*Martius' Yellow*,  $C_{10}H_6N_2O_5SNa$ , made by the action of nitric acid on  $\alpha$ -naphthol-monosulphonic acid.

*Mauvein* (hydrochloride), or Aniline Violet,  $C_{27}H_{25}N_4Cl$ , made by the action of chromic acid on aniline containing some toluidine.

*Methyl Orange*,  $C_{13}H_{12}N_3SO_3Na$ , made by the successive action of nitrous acid and methylaniline upon para-amidobenzene-sulphonic acid; it is the sodium salt of helianthin.

*Methyl Violet*,  $C_{24}H_{28}N_3Cl$ , made by oxidizing dimethyl-aniline with metallic salts.

*Methylene Blue*,  $C_{16}H_{18}N_3SCl$ , made by heating amido-dimethylaniline with sulphide of iron.

*Naphthol Yellow*,  $C_{10}H_5N_2O_8SK$ , made by the action of nitric acid on  $\alpha$ -naphthol-trisulphonic acid.

*Nigrosin*,  $C_{18}H_{15}N_3$ , made by heating aniline salts with nitrobenzene.

*Night Blue*,  $C_{33}H_{34}N_3O$  (the hydrochloride of this is the commercial dye), made by heating pararosaniline with aniline and benzoic acid.

*Pararosaniline* (chloride),  $C_{19}H_{18}N_3Cl$ , made by oxidizing a mixture of para-toluidine and aniline with arsenic acid, or nitrobenzene.

*Phenylene Brown*. — See Aniline Brown above.

*Ponceaux*, or *Bordeaux*. — Various derivatives of azonaphthalene. “*Ponceau 3R*,”  $C_{19}H_{15}N_2O_7S_2Na_2$ , is made by combining diazocymene hydrochloride with  $\beta$ -naphthol-disulphonic acid.

*Primulin*,  $C_{14}H_{12}N_2S$  (?), made by the action of sulphuric acid on thiotoluidine.

*Resorcin Yellow*, or *Tropæolin O*,  $C_{12}H_{16}N_2O_5S$ , made by the action of diazobenzene-sulphonic acid on resorcin.

*Rhodamine* (hydrochloride),  $C_{28}H_{31}N_2O_3Cl$ , made by the action of phosphorous trichloride on fluorescein, and treatment of the product with diethylamine.

*Roccellin*,  $C_{20}H_{13}N_2O_4SNa$ , made by the action of  $\beta$ -naphthol on the diazo-compound of naphthionic acid.

*Rosaniline*. — See Fuchsia above.

*Rose Bengale*,  $C_{20}H_4Cl_2I_2O_5K_2$ , made by the successive action of chlorine and iodine upon fluorescein.

*Rosolic Acid*,  $C_{20}H_{16}O_3$ , closely allied to aurin; neither aurin nor rosolic acid is specially valuable.

*Safranin*,  $C_{21}H_{21}N_4Cl$ , made by the oxidation of a mixture of tolulenediamine and aniline or toluidine.

*Tropæolin*. — This name is applied to various compounds made by the successive action of nitrous acid and phenols upon amidobenzene sulphonic acids. See Resorcin Yellow above.

*Uranin*,  $C_{20}G_{10}O_5Na_2$ , the sodium salt of fluorescein (which also see above).

*Victoria Green*. — See Malachite Green above.

*Victoria Orange*. — See Aniline Orange above.

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## THE PERIODIC LAW<sup>1</sup>

THE name "Periodic Law" is given to the generally accepted embodiment of the relations existing between the various properties of the chemical elements, so far as they can be compared with one another. It may be stated as follows: *If the elements are arranged in the order of their atomic weights, each of their properties varies as a periodic function of the atomic weight.*

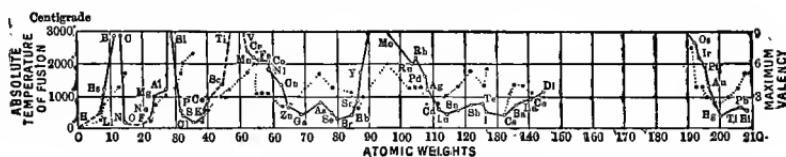
Ever since the work of Richter, Proust, and Dalton had established the idea of fixed numerical values attaching to the ingredients of compounds (an idea which was deduced by Dalton from the hypothetical existence of individual atoms, identical in size, mass and other properties for any one element), chemists sought to deduce a closer relationship between the various elements from a comparison of the masses of their respective atoms. The first attempt was that made by Dr. Prout in 1815 to prove that all the atomic weights were even multiples of the atomic weight of hydrogen, and that the latter was the only primitive element, from which the others were derived by processes of condensation. It was soon found that very few elements possessed atomic weights that could be expressed by integers, when the atomic weight of hydrogen was set at unity, and Prout's law was gradually modified to state that one half the atomic weight of hydrogen, then that one-quarter, should be taken as the real standard. Refinements of investigation have since established the relative atomic weights to the second place of decimals, and it can now be asserted that the number

<sup>1</sup> Reprinted from the *New International Encyclopædia* (Dodd, Mead & Co., New York, 1912, 15, 593-597), by permission of the Publishers.

of exact coincidences with Prout's law, as compared with that of deviations from it, is not much greater than what would be expected by the theory of chances. Prout's law, has, therefore, been practically abandoned. On the other hand, interesting relations were found to exist between the atomic weights of similar elements. Thus Doeberiner established, in 1829, his so-called triads, sets of three closely related elements whose atomic weights were approximately in arithmetical progression, as lithium (7), sodium (23), and potassium (39); calcium (40), strontium (88), and barium (136); sulphur (32), selenium (79), and tellurium (127); chlorine (35.5), bromine (80), and iodine (127); iron (56), nickel (57), and cobalt (58). These triads were later extended to include longer sets, and it was also pointed out that the constant differences were in many cases multiples of 16, the atomic weight of oxygen, whence it was assumed that the heavier elements of a group might be oxides of the lightest, thus reducing the number of primordial elements considerably. The idea of connecting all the atomic weights in a single progression wherein similar elements recurred at regular intervals seems to have first struck de Chaucourtois, and shortly afterwards Newlands; but the law in its complete form is due to Mendeléeff and Lothar Meyer, who reached the same conclusion independently in 1869. As Mendeléeff's exposition was by far the more convincing, he has been given the greatest share of the credit.

A good idea of the fundamental principle can be obtained from the accompanying figure, in which the maximum valencies in the elements and their melting-points are shown to be periodically related to the atomic weights. The latter are laid off as abscissas, and the valencies and melting-points as ordinates, on perfectly arbitrary scales. It will be seen that the two curves connecting the respective points are un-

dulatory, with well-defined maxima and minima, which occur at regular intervals. The curves for most of the other properties which are capable of precise measurement are found to have a similar character; the maxima and minima, of course, do not always coincide with the same elements in one curve as in another, but the elements which occupy similar positions on one curve are also found to be similarly located on another. It is especially noticeable, moreover, that such curves indicate a relationship between the groups of elements, as well as between the individual elements of each single group. Thus the properties of the alkaline-earth metals are always found to be intermediate between those of the alkalies and those of the aluminum group. Breaks in the continuity of the curves indicate lack of sufficient experimental data.



The arrangement of the elements, as shown in the accompanying table (p. 148), is the one generally adopted at present, and includes all the well-known elements. An asterisk marks the elements discovered since 1869. Hydrogen occupies a unique position, and is generally omitted from the classification. Argon, helium, neon, and krypton cannot be properly included as yet, because their chemical behavior is still unknown. The vertical columns include the elements most closely associated with one another, and are known as *Groups I, II, etc.*; horizontally, we have the *Series 1, 2, 3, etc.*, in which the similarities are not great, excepting that a parallelism exists between the elements of one series as compared with those of another. The elements in odd-numbered series bear a closer resemblance to one another than they do to the

elements of the intervening even-numbered series, and vice versa, so that it has been found expedient to make two divisions of each group, as will be seen in the table,— the odd-numbered series being set upon one side, the even-numbered upon the other. In the eighth group occur triplets of closely analogous elements to be discussed below. Arrangements into fifteen or more individual groups, in place of the twin and triple groups here shown, have been suggested, but not generally adopted. Mention should also be made of the fact that this table can be constructed by writing the elements in the order of their atomic weights along a screw-line of slight pitch upon the surface of a cylinder, and then, as it were, unrolling the cylinder. Various efforts have been made to connect all the atomic weights by a graphic equation, which would provide for an arrangement on some other kind of a spiral curve, either on a plane or in space, but they have been only moderately successful.

Before proceeding with a discussion of the details of the table, it may be well to inquire what significance can be attached to this periodic variability of properties as functions of the atomic weight. The many attempts to connect the atomic masses themselves in arithmetical relations would indicate a widespread opinion that the substances now called elements are really compounds of simpler substances, whose particles have a finite mass and represent individuals of distinct chemical properties, so that the chemical elements in each of the periodic groups might be likened to one of the "homologous series" of organic compounds. This view really antedates the periodic law, but fails in large measure to account for the resemblance existing between adjacent members of different groups. Many, especially Sir William Crookes, have held that the atoms are really fortuitous agglomerates of an indifferent primordial element, and that atoms of ap-

proximately the same mass behave similarly because they vibrate similarly, while atoms of greater mass might vibrate harmoniously with the smaller ones. It is difficult to explain, according to this hypothesis of the "genesis of the elements," why their number should be as limited as it is. But some facts are known, vaguely pointing to the idea that the atoms of elements within the same periodic group are capable of vibrating at harmonically related rates, and that the great majority of chemical and physical properties depend upon atomic vibrations. It may, however, be argued that just as violin-strings may be composed of different materials and yet vibrate together according to common laws, so may the elements be composed of as many individual materials and still exhibit a periodic recurrence of properties, if the latter depend upon the harmonic vibrations of the atoms. Until much additional proof has been brought, the periodic law, while furnishing a vague indication, cannot be taken as positive evidence of the qualitative unity of matter.

In the table it will be found that the first group contains the univalent elements, the second group those which are divalent, and so on up to the seventh, where the maximum valency is seven. The maximum valency of the elements of the eighth group may be set at eight, but their compounds rarely exhibit so high a valency, and in many other respects this eighth group is rather anomalous and is taken as a transition group between the seventh and the first. Thus the three elements, copper, silver, and gold belong, with respect to many of their properties, especially when uncombined, in the eighth group; but their valency is usually low, and many of their salts are so similar to those of sodium that it is often found expedient to place them in the first group, in the positions occupied in the table by their names inclosed in parentheses. The valencies refer especially to the stable oxides. Stable compounds

PERIODIC ARRANGEMENT OF THE ELEMENTS ACCORDING TO INCREASING ATOMIC WEIGHTS

Serial No.	Groups I	II	III	IV	V	VI	VII	VIII			
								a	b	c	d
1	Hydrogen 1.008					Nitrogen 14.	Oxygen 16.	Fluorine 19.			
2	Lithium 7.	Guanium 9.1	Boron 11.	Carbon 12.		Phosphorus 31.	Sulphur 32.07	Chlorine 32.46			
3	Sodium 23.	Magnesium 24.3	Aluminum 27.1	Silicon 28.4		Vanadium 51.4	Chromium 52.1	Manganese 55.	Nickel, 58.7	Cobalt, 59.	Copper 63.6
4	Potassium 39.1	Calcium 40.	Scandium* 44.1	Titanium 48.1		Arsenic 75.	Selenium 79.2	Bromine 79.9			
5	(Copper) 63.6	Zinc 66.8	Gallium* 69.9	Germanium* 72.5		Zirconium 90.4	Colombium 98.7	Molybdenum 98.	Ruthenium, 101.7	Rhodium, 103.	Palladium, 106.4
6	Rubidium 85.4	Strontium 87.6	Yttrium* 8.9			Tin 119.	Antimony 121.4	Tellurium 127.5?	Iodine 126.9		Silver 107.9
7	(Silver) 107.9	Cadmium 112.4	Indium 113.8			Cerium 139.4	Praseodymium* 140.6	Neodymium* 143.9			
8	Cesium 132.9	Barium 137.4	Lanthanum 138.9								
9											
10				Erbium 166.3			Tantalum 168.8	Tungsten 184.8	Osmium, 191.	Iridium, 193.1	Platinum, 194.9
11	(Gold) 197.2	Mercury 200.	Thallium 204.1			Lead 206.9	Bismuth 206.1				
12						Thorium 232.6	Uranium 239.6				

of hydrogen occur only in the fourth, fifth, sixth, and seventh groups, four atoms of hydrogen combining with one of each element of the fourth group, and this amount decreasing until we find the halogens in the seventh group univalent toward hydrogen. The first group includes the most electro-positive elements, and there is a steady transition toward the electro-negative end of the series in the seventh group, while the eighth group shows a rather sudden return toward the electro-positive side. The majority of the compounds derived from elements at the left end of the table are soluble, colorless, and volatile, whereas these properties change from left to right until we find the maximum of insolubility, color, and resistance to heat in the lower right hand of the table. It is also possible to select analogous compounds of the different elements and find those of similar properties falling within a well-marked zone upon the chart. Mendeléeff, in his original essay, added the following: (1) The elements which have the lowest atomic weights are those most widely distributed in nature, and also represent the most typical characteristics found in the second series of the table; (2) the atomic weight determines the character of an element; (3) from a consideration of their position in the system new analogies can be discovered between elements; (4) it may be expected that new elements should be discovered to fill blank spaces within the table, and their properties can be predicted from a consideration of those of the adjacent elements; (5) errors in the assumed atomic weights may be detected through an irregularity in the position of the element in the periodic system.

All of these statements have been verified, and the immediate acceptance of Mendeléeff's views was facilitated especially by the sensational discovery of a number of elements whose properties agreed accurately with those predicted by Mendeléeff. Thus gallium, germanium, and scandium had been completely described with respect to their

own properties and those of their compounds before they were actually discovered. Success has also attended the attempts to correct atomic weights in several cases where the elements appeared misplaced in the original tables and were assigned to positions more in accordance with their properties, but necessitating the assignment of new atomic weights. The weakest point of the table lies in the position of tellurium, which should fall into the sixth group, but is found to have a higher atomic weight than iodine, which undoubtedly belongs to the same series in the seventh group. Efforts to explain this discrepancy have so far been unavailing. There are also a number of elements derived from the so-called rare earths whose place in the system is not readily assignable. In the latter case, however, it may be said, as well as in that of the atmospheric gases, argon, helium, neon, and krypton, that their properties and atomic weights are not so well established as to cast doubt upon the theory through their failure to coincide with it. One interesting result of the theory is that of limiting the probable number of chemical elements to about 120, since the actual number of blank spaces is limited, and since it is extremely unlikely that any elements remain to be discovered with an atomic weight less than that of hydrogen or greater than that of uranium.

Among the *physical properties* which appear as periodic functions of the atomic weight may be mentioned the densities of the uncombined elements and of their oxides, fusibility, atomic volume, crystalline structure of the compounds, coefficient of expansion, refractive index, conductivity for heat and electricity, color, and velocity as ions.

As an indication of some purely *chemical periodicities* the following conspectus has been arranged, in which the elements are indicated by their positions in the above table, and are generally enumerated in such order that the one which shows the property in the most marked degree has precedence. The

maximum valency of the elements toward *oxygen* is indicated throughout by the Roman numeral of each group, omitting the "peroxides," in which the oxygen appears to be linked in a different manner.

Maximum valency toward hydrogen in stable volatile compounds: —

Univalent: VII; 2, 3, 5, 7; powerfully acid hydrogen compounds.

Divalent: VI; 2, 3, 5, 7; faintly acid hydrogen compounds.

Trivalent: V; 2, 3, 5, 7; basic acid hydrogen compounds.

Quadrivalent: IV; 2, 3, 5; neutral acid hydrogen compounds.

Maximum number of hydroxyls in basic compounds: —

One: I; 1, 2, 3, 6, 8. III; 11. VIII; 6 (c and d).

Two: II; 2, 4, 6, 8, 3, 5, 7, 11. IV; 11. VIII; 4 (bcd).

Three: III; 3, 4, 5, 6, 7, 8, 10, 12. V; 11. VII; 4. VIII; 4a.

Minimum valency in oxygen acids: —

One: VII; 3, 5, 7.

Three: V; 2, 3, 5, 7. VI; 3, 5, 7.

Four: IV; 2, 4, 3, 5, 7, 11.

Five: V; 4, 6, 10.

Six: VI; 4, 6, 10. VII; 4. VIII; 4a.

Tendency to liberate hydrogen from water below red heat: —

I; 2, 3, 4, 6, 8. II; 2, 3, 4, 6, 8. VIII; 4a.

Tendency to liberate oxygen from water: —

VII; 2, 3, 5.

Elements whose chlorides are unstable toward water: —

V; 3, 5, 7, 11, 4, 6, 10, 12. VI; 10, 6, 4.

Elements whose sulphides can be precipitated from dilute acid solution: —

VIII; 4d, 6 (abcd), 10 (abcd). II; 11, 7. III; 11, 7. IV; 11, 7, 5.

V; 11, 7, 5. VI; 12, 10, 6.

Ability to form alums with the sulphates of I; 2, 4, 6, 8: —

III; 2, 4, 6, 10. VI; 4. VIII; 4a.

Ability to form volatile compounds with organic radicles: —

With one methyl group: I; 3. VII; 2, 3, 5, 7.

With two methyl groups: II; 3, 5, 7, 11. VI; 2, 3, 5, 7.

With three methyl groups: III; 2, 3, 5, 7, 11. V; 2, 3, 5, 7, 11.

With four methyl groups: IV; 2, 3, 5, 7, 11.

Ability to form complex bases with ammonia: —

VIII; 4 (cd), 6 (abcd), 10 (abcd). VI; 4. II; 3, 11.

Consult: Newlands, *On the Discovery of the Periodic Law and on Relations Among the Atomic Weights* (London, 1884); Huth, *Das periodische Gesetz der Atomgewichte und das natürliche System der Elemente* (Frankfurt a. O., 1884); Belar, *Das periodische Gesetz und das natürliche System der Elemente* (Laibach, 1897); Mendeléeff, "The Principles of Chemistry," in *A Library of Universal Literature* (New York, 1901); Venable, *The Development of the Periodic Law* (Easton, Pa., 1896).

## THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY<sup>1</sup>

WITHIN a few weeks will occur an event of supreme importance to American chemists and especially to those interested in the branches of our science to which this Journal is especially devoted:—the meeting, in Washington and New York, of the International Congress of Applied Chemistry. Strictly speaking, this is not the first time that such an organization has met on American soil, since the first impetus to the plan of these international meetings seems to have been derived from the sessions of foreign and American chemists who attended the Columbian Exhibition in Chicago in 1893. Every World's Fair has, in recent years, been accompanied by meetings of specialists in sciences and arts; but it must be remembered that they bear the relation of what is popularly called a side-show to the Exhibition itself. They are more or less haphazard in their relation to the general world of science, and there is no continuity of management from one occasion to the next. The various international scientific congresses are autonomous; the experiences gathered at one meeting are utilized in the preparation for the next one; special problems are committed to the care of qualified experts, for the report of authoritative opinion to the next gathering, and the way is paved for that general world-wide coöperation in the advancement of knowledge and the perfection of its utilization, which has been within narrower limits the chief virtue of the various national organizations.

It is just two hundred and fifty years since the Royal

<sup>1</sup> Editorial, reprinted from *Journ. Ind. and Eng. Chem.*, p. 556, 1912.

Society was incorporated in London, — with the sole exception of the Accademia dei Lincei, probably the oldest existing society for the exchange of knowledge between the devotees of exact and natural sciences. For nearly two centuries these societies were not only close corporations but also practically local clubs. The greater diffusion of scientific learning, as well as the increased means of communication by railroad and telephone, led to the establishment of national associations for the advancement of science (with more liberal terms of membership) having the added feature that meetings were never held twice in succession in the same city. A natural outgrowth was the national society for the promotion of some particular science. Since increased specialization soon made it impossible for anybody to follow understandingly the sessions of general associations, these met in sections — a circumstance which led to the development of a yet closer form of union among their respective members.

Thus, in chemistry at least, each great nation now possesses one or more special societies, not restricted as to localities or qualifications, as is the case with the academy or institute, but open to every person interested in the science. At the last annual meeting of the American Chemical Society there were assembled as many members as would have been deemed a fair attendance for the entire American Association for the Advancement of Science, not very many years ago. It is unnecessary to descant here on the advantages of oral discussion, supplemented by the pleasures of social intercourse, which make these general sessions so attractive, any more than it is important to point out the same gregarious instinct, which has led to the successful institution of so many local sections, with their well-attended stated meetings. But we must emphasize the fact that *local* chemical societies led a very precarious existence until the more powerful national

organization enabled them to gather strength by coöperation and let them experience the stimulus of generous rivalry.

And now we have entered into a new era, practically with the opening of the twentieth century, that of the utter abolition of national boundaries so far as scientific endeavor is concerned. A new chemical discovery in Paris is known in London, New York and Tokio in far less time than was consumed in the transmission of Priestley's or Cavendish's communications to the Royal Society in London, and the time is rapidly passing when the possession and guarding of a scientific secret could be deemed a national advantage. If it be deemed conducive to international amity that the young men of all nations should meet at the Olympian games, in contests of brawn and motor-nerves, how much more important is it that there be occasional interchanges of thought and knowledge! And yet, we wonder whether the press of New York will afford as many paragraphs to the forthcoming International Congress of Applied Chemistry, for matter supplied to it free of expense, as it has published pages of expensive cablegrams from Stockholm? We do not expect any mobs of frenzied cheerers to throng around the arena of scientific debate; and yet we know that the impression which our foreign visitors will take home of the progress in American science and scientific industry will be of far greater importance to the esteem in which our country will be held abroad, than the number of cups which the "Finland" will bring home from Stockholm. Our individual responsibility in this Congress is as great as our individual opportunity.

To meet the leaders of chemical knowledge and of chemical manufacture, from abroad as well as at home, to listen to a free exchange of thought and practical experience, are privileges for which innumerable chemists have traveled to Berlin, London, Paris, Vienna, and Rome. We all now have these chances

at home, coupled with the opportunity to benefit by free and generous criticism of whatever we may desire to bring to their view. In chemical industry, at least, mediæval secretiveness is breaking down in favor of frank exchange of experiences.

That the scientific importance of the approaching Congress is thoroughly realized may be gathered from the fact that upwards of six hundred papers have already been accepted and are being printed, ready for distribution at the Congress itself. In view of the stringent rules of acceptance which have been adopted, and the early date set for the submission of the papers themselves, it would probably have been easier for the authors to secure publication in the journals of their respective national chemical societies, had they not recognized the paramount claims of this international scientific gathering.

The American committee of arrangements is bending every effort toward making the sessions agreeable to the participants; they are particularly anxious to make this Congress memorable for the promptness with which it shall transact its business, the smoothness with which the machinery of entertaining its members shall revolve and the completeness with which their comfort may be considered. This means as full coöperation on the part of every American chemist as has been cheerfully afforded by the hard-working members of the various committees. It may be taken for granted that every chemist who can get away from his work, no matter in what part of the United States he resides, will be anxious to attend the Congress, not only for the selfish reasons already stated, but also for the patriotic one of adding by his own presence to the prestige of the greatest chemical function which is likely to occur here for many a year. . . .

## CHEMISTRY AND CIVILIZATION<sup>1</sup>

THAT invention is one of the chief factors in the world's progress, and that scientific investigation is at least coördinate with geographical discovery in widening the bounds set to human comfort and well-being, are assertions which may well be called axiomatic. To discuss the influence of scientific discovery upon civilization might seem a sort of supererogation, a mere rhapsody on man's wit and energy; even the slightest hint that all invention has not made for progress, industrial or cultural, may possibly be taken as the mark of black pessimism or whimsical conservatism. Yet no other chain of events has proven, on nearer view, to have maintained a single direction; and that historian is not deemed unpatriotic who recites impartially the failures as well as the successes in his country's record, especially if a study of the darker phases may lead to an avoidance of future pitfalls. Thus, too, not every scientific theory or practical invention must necessarily have been in the line of real progress; some may have led to the squandering of nature's bounty, or perhaps to the temporary disregard of some more important line of research. It may, therefore, be both fruitful and instructive to attempt a closer study of the ultimate, as well as the immediate effects of such innovations; besides obtaining a more stereoscopic picture of an important branch of human activity, we may derive some useful lesson, at a time when the gradual exhaustion of the earth's stored wealth is giving food for anxious thought. In attempting to measure

<sup>1</sup> The unfinished introduction to a projected treatise; found in manuscript, 1912.

the effect of a scientific invention upon civilization, we must proceed rather differently than would the historian of philosophic or religious, economic or political, development. In exact science, at least, no hypothesis can be so erroneous as to work practical harm, except possibly by retarding the adoption of a correcter view; and who would try to estimate the amount of such retardation? Based upon the observation of solid facts, a hypothesis is accepted so far as it seems to connect them with one another, but receives scant attention so long as it does not lead to equally positive results. A false ethical, economic or political theory may enjoy universal credence for generations, before its evil effects upon the commonwealth shall have been recognized and corrected by what is usually termed reformation or revolution. Scientific *thought* has a scarcely perceptible influence upon a people; it is the *practice* by which they are helped or harmed. For this reason, the scientific discoverer must be content to see his work popularized by the inventor, and the Wollastons, Henrys and Hertzes are unknown to those for whom Daguerre, Edison and Marconi are household words.

The influence of a scientific invention, put to practical use, may be felt in various directions: it may assist the culture of the individual, by opening up new channels of thought or providing new means of æsthetic enjoyment; it may increase our physical comfort, by placing in our hands new weapons wherewith to combat hunger, disease, heat, cold, and other elemental forces; it may modify the intercourse of individuals and peoples, by devising new modes of communication and transportation; it may dislocate political relation, by creating more potent engines of offense or defense; it may, temporarily at least, profoundly alter the commercial prosperity of whole provinces, creating new sources of wealth in one locality, and depreciating the product of another; finally, it may

have a share in determining the entire problem of the possibility of human existence upon this earth, on the one hand by promoting a more efficient utilization of natural resources, on the other, by inducing us to squander futilely, within a lifetime, material that has been accumulated during untold ages. Rarely will close analysis permit the conclusion that an invention has wielded only one kind of influence; seldom will no interest be found to have suffered from something that has produced profit and enjoyment for the multitude; practically never, I firmly believe, has the evil preponderated so largely over the good, that a corrective could not be applied in time to prevent an irremediable harm. And yet, the popular mind is far from applying true standards to the estimate of certain inventions, that have been hailed as the achievements of our era.

Let me recite a few examples, in illustration of my last assertion, without treating them as fully as if they came entirely within the scope of my inquiry.

Is it not generally conceded that the tremendous gain in individual efficiency, derived from the introduction of telegraph and telephone, is offset to a greater or lesser extent by an increased nervous irritability and decreased vitality? Has not the diffusion of knowledge, through the introduction of the power press, with the consequent cheapening of printed matter, been accompanied by the virtual submergence of good literature under a flood of ephemeral reading-matter; just as the typewriter, with all its advantages, is surely undermining the elegance of our diction? All these and kindred inventions have vastly facilitated talking to our fellow-men; have they improved the quality of our conversation or strengthened our thinking-processes? We can deny this without wishing [for one moment that these potent aids to communication had not been invented.] . . .

Dismissing, as incidental to a mere plaything, the reckless disregard of public safety, as well as the bad manners of the "speeder," ought we not to realize that the undoubted enjoyment and practical convenience of automobiling requires for the locomotion of the single individual an utterly disproportionate amount of energy, whether we measure it in the conventional horse power, or in the stored-up solar energy represented by the petroleum burnt up for the propulsion, and the ores, coal, and gums utilized for the construction of this modern conveyance?

Perhaps the motion-picture, as an instrument for entertainment and instruction, is too novel to justify an estimate of its good and evil effects; some hail it as a potent aid to education, while others invoke the police to curb its power to promote immorality and vice. It is thought a dangerous competitor to the theatre; though we may well doubt whether its rivalry will be felt by the higher drama so much as by the vaudeville and melodrama, whose decay can hardly be deplored. But the economic influence of these cheap and all-pervasive picture-shows has yet to be estimated, both in the amount of money extracted from that portion of the population which can least afford it, and in the hours diverted from more healthful recreation, as well as from gainful occupation.

Coming to a far more serious problem of world-wide import, we have the installation of those modern means of transportation which have so vastly extended the distance from which we can derive food and commodities. It would, of course, require years of study by a trained economist to evaluate all the effects upon commerce, as well as upon the subsistence of urban and rural population, which have resulted from the gradual removal of the grain-farmer and stock-raiser from the neighborhood of the consumer. The sociologist, on

the other hand, must recognize the difficulty of the task of tracing the influence of these causes in encouraging the concentration into large centers, in depleting the older rural communities of their more energetic elements, and in eliminating, more or less completely, that element of the village community which formed the connecting link between city and country life of the past; while he hails the gradual extension of the benefits of civilization over the entire earth. Popular opinion, pointing to the reduced price of food-stuffs, clothing and other comforts, to the freedom of migration for the individual, the wage-earning opportunities for the myriads employed in the carrying trades, will unhesitatingly answer in the affirmative any question as to the value of these modes of communication. Public opinion on this topic will doubtless be justified at that time, when the increased population of the earth will demand the exploitation of all its resources, the tilling of every arable field, the harnessing of every horse-power.

At the present juncture, however, the physicist cannot join the chorus of praise, until he has satisfied himself on certain points that come more closely within his ken. For him, money as a standard of comparison must ever be secondary to the amount of energy, — in the dynamic sense, — requisite for the attainment of a desired object. So far as this energy has a market value, as in the wages for day-labor or in the price of fuel, coin may form a temporary expedient for casting a balance, — less reliable, I fear, than most schools of political economy will admit.

I have been struck, comparing the prices of certain staple commodities, as a bushel of wheat, a cow, a work-horse, with a laborer's wage in ancient Jerusalem, imperial Rome and modern New York, by the apparent constancy of the ratios, which might well lead us to look to departures from such a

fixed mean, — whether we estimate them in gold or in day's work, — as the true measures of the fluctuation in mundane prosperity. But if we go to over-populated China and barely-settled Alaska, we note such astounding dislocations of these proportions, that we realize to what extent their apparent constancy is predicated upon the equilibrium between natural resources and man's demand thereon; or rather, upon such a superabundance of these resources, that human consumption does not noticeably affect them. During the twenty-five or thirty centuries of historic times preceding the nineteenth this condition was maintained. Our forefathers drew their sustenance from the surface of the earth and consumed rather less than was derived from the solar energy during their respective lives. In the nineteenth century commenced that wholesale exploitation, which has drawn in ever-increasing quantity upon the stored-up riches of the earth's interior. So that within the last thirty years we have been forced to recognize that the future progress, if not existence, of the human race is threatened by the gradual exhaustion of our supplies of food and fuel. Even that most unreasoning optimist, the American politician, prates of the importance of conserving our natural resources.

The great break in the continuity of dynasties and nations which the historian entitles the French Revolution coincides more or less closely with that still more portentous change in human history, the substitution of mechanical methods of manufacture for handicraft. Simultaneously began the development of chemical factories to which the historian has paid no attention, though its effect reached further than even the political economist ordinarily can recognize. There were countless revolutions before the one which dethroned Louis XVI, and man had learned to harness animals, wind and water to replace his own meagre forces, and had shaped

tools and built machines, many centuries before the birth of Watt and Arkwright. Just so, many operations that involve a change of substance, and are therefore properly classed among chemical processes, had their origin in prehistoric times. Ore-smelting, tanning, dyeing, the making of cement, pottery and glass are good examples of industries now peculiarly within the chemist's control, but which were practiced by rule of thumb, by skilled artisans, ever since the dawn of civilization.

Then, again, the preparation of perfumes and cosmetics, medicines and poisons, had been perfected long before the Roman era, and these arts were preserved by Jews and Arabs during the barbarous relapse of mediæval Europe; so that there was a constant development, from the magic of the Egyptian priesthood, through the alchemy of a Geber and an Albertus Magnus, the spagirism of a Paracelsus and a Glauber, to the chemistry of a Becher and a Boyle. By the middle of the eighteenth century, scientific chemistry had reached a point where it could give a rational explanation of some of the industrial processes of the period, and could seek to control their operations by distinct tests and to improve them upon the basis of laboratory experiments. But the essential step toward the domination of scientific theory over empirical manufacture was taken when Bergman, Lavoisier and their contemporaries recognized the constant quantitative composition of chemical substance; for now it became certain that the proportion of ingredients which proved most advantageous in a laboratory experiment must be the ratio to which the manufacturer should adhere; the percentage of useful substances contained in raw materials from various sources could be estimated. At times it would be discovered that certain admixtures, prescribed for centuries by traditional formularies, contributed nothing to the desired com-

pound, and could be omitted with the same impunity as could the magic incantations of the alchemists.

Lavoisier perished in the French Revolution; but this same political upheaval gave an indirect impetus to chemical manufacture in the modern sense. For the ensuing wars, with their commercial reprisals which cut off both France and England from their existing sources of supply, stimulated attempts to substitute artificial for natural commodities, and the governments offered premiums for the invention of processes which would manufacture articles at home that were heretofore imported from the colonies or abroad. Hence arose the beet-sugar industry, and the Leblanc process for making artificial soda, to replace the ashes of wood and seaweed no longer available in sufficient quantities for the making of glass, soap, etc. The Leblanc process, however, called for a plentiful supply of cheap sulphuric acid and liberated large quantities of hydrochloric acid, for which an outlet was found in the production of chlorine and bleaching-powder for the textile industries. To this day, soda manufacture and its allied induction may be considered the foundation of all chemical technology, of which the beet-sugar process is the first example of the production in bulk of an organic compound by a complicated series of steps which could never be carried on successfully on a small scale. Up to the end of the eighteenth century, chemicals were made by the pound, since then by the ton.

Of course, many other causes have succeeded this political impetus as stimulants to chemical industry: — mechanical inventions, in connection with the employment of steam as a motive power; the influence of railroads and steamships in facilitating the collection of raw materials and finished products; the discovery of great ore-bodies, of petroleum fields and vast coal-beds; finally, the conversion of mechanical

force into electricity, whereby water-power, the next derivative of solar energy, becomes available as a constant source of light, heat and chemical action.

Coal, petroleum, natural gas and ores have accumulated within the earth's crust for untold ages. Mankind commenced to draw upon this supply during the past hundred years and is already considering anxiously its approaching exhaustion. Chemistry, which has played the leading part in this sudden increase of consumption, is largely concerned in the effort to restore the balance which has been disturbed.

With justifiable confidence, we pin our faith upon the progress of scientific discovery and invention. We should not, however, do this blindly, but seek to estimate our present accomplishments at their true value. This is what I have set out to do in the present volume,<sup>1</sup> not, indeed, with the hope of presenting an exhaustive treatise, but of stimulating thought in this direction and of leading to a closer inquiry into the steps by which legislation might differentiate the industries which promote from those which might endanger the public good.

For this purpose, I intend to follow up the ramifications of the chief industries affected by chemical research and attempt to trace their influence upon human welfare, partly by ascertaining what facilities they have afforded, partly by estimating what consumption of energy they have entailed, and partly by showing what older industries they have displaced or effaced. . . .

Local conditions, legislation, trade and labor combinations have so much more effect upon wages and living-conditions of the laborer, than has the progress of technical science, that this subject may be deemed outside of the pre-

<sup>1</sup> One cannot but feel poignant regret that the rest of the volume was never written.  
[EDITOR.]

sent field. The sanitary side of factory-life must, however, be considered, from time to time, since it is indeed important to know whether we are enjoying certain luxuries and comforts at the risk of life and happiness of our fellow-men; we must surely count the cost of human life as seriously as the expenditure of fuel and horse power.

In most chemical industries, even taking into account special risks from poisoning and explosions, hygienic conditions are probably above the average factory standard. In Germany and other enlightened countries, intelligent legislation regarding sanitation and employers' liability has wonderfully diminished those "unavoidable accidents" which crowd the American news columns, and has reduced the toll in deaths, sickness and lessened vitality, which unfettered industrial competition still exerts in our own country. Excepting in a direct tussle with nature, there should be far fewer really hazardous occupations; certainly, the dangers connected with chemical manufacture are so well known that the proper precautions should be readily available.

On the other hand, it will hardly be profitable to estimate accurately the question of the influence of chemical manufacture in accelerating the much-deplored flow of rural population to the cities. Doubtless, every factory attracts an additional force of laborers, and the aggregate pay-rolls of chemical factories must contain an enormous number of potential farmers. For instance, it has been said of the beet-sugar factories that they constitute the most natural transition from farm to factory work; a statement which is apt to be contradicted by those who have seen farmers' children thronging the cotton-mills and shoe-factories of New England. It will be admitted by those who deplore the townward trend, that chemistry has somewhat atoned for the laborers whom it

has lured away from the farm by its gift of artificial fertilizers and by the increased market which it has provided for various farm-products. . . .

[The manuscript ends here, although the essay was evidently not completed.]

## **PART II**

### **ORIGINAL EXPERIMENTAL INVESTIGATIONS**



# UEBER DIE EINWIRKUNG VON PHOSGEN AUF AETHENYLDIPHENYLDIAMIN<sup>1</sup>

VON Hrn. Prof. HOFMANN veranlasst, habe ich die Einwirkung des Phosgens auf Aethenyldiphenyldiamin studirt und bin vorläufig zu folgenden Resultaten gekommen.

Die genannte Base wurde mit flüssigem oder in Benzol gelöstem Phosgen 8–10 Stunden im Einschlussrohr auf 80° erhitzt. Das Rohr zeigte nur geringen Druck, in der Reaktionsmasse hatte sich viel Anilinchlorhydrat ausgeschieden; mit Benzol und Aether konnte eine Substanz isolirt werden, welche aus Alkohol in Krystallen anschoss.

War mehr als 1 Mol. Phosgen auf 2 Mol. Base angewandt worden, so enthielt das Produkt Chlor, bildete kleine Nadeln und schmolz bei 110°; es gab bei der Analyse Werthe, welche auf die Formel: —



stimmen: —

	Berechnet:	Gefunden:
C	57.31	57.34 pCt.
H	3.58	3.61 "
N	8.35	8.46 "
Cl	21.19	21.54 "

Eine derartig zusammengesetzte Verbindung wird entstanden sein nach der Gleichung:  $\text{C}_{14}\text{H}_{14}\text{N}_2 + 2 \text{COCl}_2 = 2 \text{HCl} + \text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ .

Stellte sich das Molekularverhältniss zwischen ange-

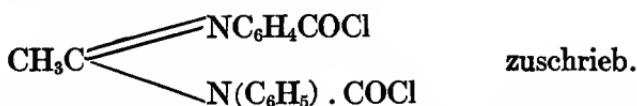
<sup>1</sup> Vorläufige Mittheilung. *Berichte d. deutsch. chem. Gesellsch.* [hereafter designated as *Berichte*] 18, 2427 (1885). Aus dem Berl. Univ.-Laborat. No. DCII. Eingegangen am 15. August.

wandter Base und Phosgen auf 4:1, so wurden chlorfreie, bei 115.5° schmelzende, derbe Nadeln oder fächerförmig angeordnete Blättchen aus Alkohol erhalten, deren Analyse auf einen Harnstoff der Formel CO. $(C_{14}H_{18}N_2)_2$  deutet.

Mit der genaueren Untersuchung der genannten Produkte, sowie mit den Studium der Einwirkung des Phosgens auf Guanidine und Urethane bin ich noch beschäftigt.

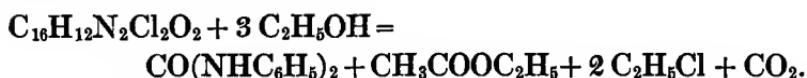
## UEBER AMIDINDERIVATE<sup>1</sup>

VOR einiger Zeit<sup>2</sup> habe ich über einen Körper berichtet, welcher durch Einwirkung überschüssigen Phosgens auf das Aethenyldiphenyldiamin entsteht, und welchem ich, auf Analysen gestützt, die Formel —



Ich habe seitdem diese Annahme durch Darstellung eines entsprechenden Esters bestätigen können; zur Bildung anderer Derivate [2341] war bei der Beständigkeit jenes Körpers leider nicht zu gelangen. Schon bei der Darstellung und Reinigung des Chlorides ist es geboten, eine Temperatur von 60° nicht zu übersteigen, wenn man eine Ausbeute, die bei niedriger Temperatur 60 pCt. betragen kann, nicht erheblich verringern will.

Von kochendem Wasser wird das Chlorid nicht angegriffen, von Säuren und Alkalien dagegen in das Amidin zurückverwandelt; mit siedendem Alkohol liefert es Carbanilid, Essigester und Chloraethyl.

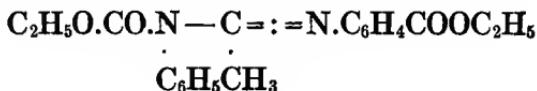


Bei der Darstellung eines Esters muss jede Erwärmung vermieden werden. Natrium (2 Atome) wurde in Aethylalkohol gelöst, und nach dem Erkalten die alkoholische Lösung des Chlorides (1 Molektil) allmählich unter Abkühlung hinzugesetzt. Von dem sich sofort abscheidenden Kochsalz

<sup>1</sup> Aus dem Berl. Univ.-Laborat. No. DCLII, *Berichte*, **19**, 2340 (1886). Eingegangen am 14. August.

<sup>2</sup> *Berichte*, **18**, 2427 (1885) (page 169 of this book).

abfiltrirt und über Schwefelsäure im luftleerem Raume verdunstet, hinterliess die Flüssigkeit eine chlorfreie Substanz, welche nach zweimaligem Umkristallisiren aus Aether harte, glänzende, rhombische Krystalle bildet, die bei 90.5° schmelzen. In alkoholischer Lösung ist sie auch in der Kälte wenig beständig. Sie besitzt die Formel



$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4$	Verlangt:	Gefunden:		
		I	II	III
C	67.79	67.74	—	— pCt.
H	6.21	6.84	—	“
N	7.91	—	8.51	8.60 “

Derselbe, oder ein ähnlicher Körper stand bei der Behandlung des Amidins mit Chlorkohlensäureäthylester zu erwarten. Eine Einwirkung findet jedoch erst bei 60° statt; nach Verdunsten der vom salzauren Amidin befreiten Flüssigkeit verbleibt eine halbfeste Masse, welche an Aether kleine Mengen eines nicht krystallisirenden Oeles abgiebt, und im Uebrigen aus Carbanilid besteht.

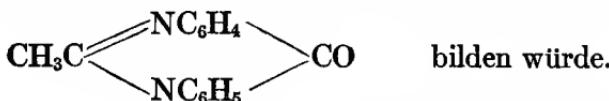
Sowohl das Chlorid als der Ester werden durch Erhitzen mit wässrigem Ammoniak in das Amidin zurückgeführt. Alkoholisches Ammoniak wirkt wie reiner Alkohol. Wird das Chlorid in Benzol gelöst, und trockenes Ammoniakgas hindurch geleitet, so scheidet sich die theoretische Menge reinen Salmiaks aus. Die Lösung enthält Aethenyldiphenyldiamin. Die Umsetzung muss also folgendermaassen verlaufen sein: —



Analog entstehen mit heissem Anilin das Amidin, salzaures Anilin und Carbanilid. Da such nun eine Amidover-

bindung aus dem [2342] Chlorcarbonylderivate des Amidins nicht darstellen liess, bemühte ich mich eine directe Anlagerung von Cyansäure resp. Rhodanwasserstoff an das Amidin, welche zu ähnlichen Körpern geführt hätte, zu bewerkstelligen. Auch diese Versuche schlugen fehl, da das Cyanat des Amidins schon in kalter, wässriger Lösung Kohlensäure und Ammoniak abspaltet; das Rhodanat, welches ein Harz darstellt, ist zwar beständiger, lagert sich jedoch nicht in den Thioharnstoff um, sondern verwandelt sich oberhalb 100° in ein übelriechendes Oel.

Aethenylimidobenzanilid. Wird das oft erwähnte Chlorid über seinen Schmelzpunkt erhitzt, so tritt bei 150° eine reichliche Entwickelung von Phosgen ein. Es schien nicht unwahrscheinlich, das sich unter den Umständen der Körper



Allein das stete Abspalten von Phenylcyanat verhinderte mich denselben hierbei zu isoliren. Es ist mir aber gelungen, ihn auf andere Weise darzustellen. Er entsteht nämlich, wenn Phosgen in Benzol gelöst, auf einen Ueberschuss von Aethenyldiphenyldiamin bei 80° einwirkt, oder wenn es als Gas durch eine siedende Chloroformlösung des letzteren geleitet wird. Er ist in Aether, Alkohol, Chloroform und Benzol löslich, und krystallisiert besonders aus letztgenanntem Lösungsmittel in grossen glänzenden Tafeln vom Schmelzpunkt 118°.

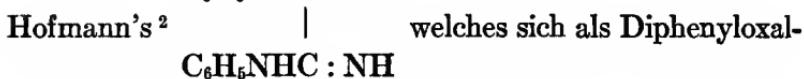
Die Formel C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O wird durch die Analyse bestätigt.

	Verlangt:		Gefunden:			pCt.
	I	II	III	IV		
C	76.27	77.33	76.61	—	—	"
H	5.08	5.62	5.60	—	—	"
N	11.85	—	—	11.73	12.07	"

Diese Substanz ist identisch mit derjenigen, welche ich früher<sup>1</sup> erwähnt und damals als bei  $115.5^{\circ}$  schmelzend angeführt habe. Ueber den Schmelzpunkt erhitzt bräunt sich das Aethenylimidobenzanilid bald, und entwickelt etwas Isonitril. Mit verdünnter Salzsäure gekocht spaltet es sich vollkommen, wobei Anilin und Phenylcyanat auftreten:—



Versuche über die Einwirkung von Phosgen auf Benzenyl-diphenyldiamin führten zu keinem Ziele, da die Reaktionsproducte allzu geringe Krystallisationsfähigkeit zeigten; die schwierige Darstellung und geringe Haltbarkeit der meisten in der Literatur verzeichneten [2343] Amidine hielten mich davon ab, die nicht besonders ergiebige Untersuchung auf solche auszudehnen. Dagegen habe ich aus dem Cyananilin



amidin auffassen lässt, durch Einwirkung von Carbonylchlorid einen krystallinischen Körper erhalten, auf welchen ich später zurückzukommen hoffe.

Ich möchte hier noch über einen Versuch berichten, Cyan an Aethenyldiphenyldiamin anzulagern. Eine gesättigte ätherische Lösung von Aethenyldiphenyldiamin, mit 2-3 Tropfen Wasser versetzt, färbt sich beim Durchleiten von Cyangas allmählich dunkel. Unterbricht man das Einleiten, sobald die Flüssigkeit weinrot geworden, und lässt sie ungefähr 16 Stunden stehen, so ist sie noch bedeutend nachgedunkelt und der Geruch des Cyans demjenigen der Blausäure gewichen. Zuweilen haben sich auch schwarze Krusten an den Wänden des Gefäßes abgesetzt. Von diesen wird

<sup>1</sup> *Berichte*, **18**, 2427 (1885) (page 169).

<sup>2</sup> Hofmann, *Liebigs Annalen*, **66**, 129 (1848); **73**, 182 (1850).

abfiltrirt, der Aether bei möglichst niedriger Temperatur verdunstet und der klebrige, braune Rückstand mit kaltem, verdünnten Alkohol vom färbenden Harze befreit. Das verbleibende, weisse, krystallinische Pulver, welches zwischen Filtrirpapier möglichst abgepresst und über Schwefelsäure getrocknet wird, löst sich sehr schwer in kaltem Aether und Benzol. Es lässt sich nicht umkrystallisiren, da es beim Erhitzen in Lösungsmitteln rasch verharzt; mit Alkohol benetzt, zersetzt es sich sogar schon an der Luft. In reinem Zustande schmilzt es unter Zersetzung bei  $165^{\circ}$ , wird jedoch schon gegen  $120^{\circ}$  violett und dann braun.

Die Analyse ergiebt Zahlen, welche sich auf einen Körper  $C_{16}H_{18}N_4O$  beziehen lassen.

	Gefunden:				
	I	II	III	IV	V
C	68.57	68.24	—	—	68.52
H	5.71	5.24	—	—	5.84
N	20.00	—	19.55	20.32	—
					68.6 pCt.
					“

Diese Formel lässt sich am einfachsten nach dem Vorbild von Griess' Cyancarbimidoamidobenzösäure<sup>1</sup> und von Bladins Cyanphenylhydrazinderivaten<sup>2</sup> in folgender Weise deuten:—



Ich gedenke den Körper weiter zu untersuchen. [2344]

Zum Schlusse mag hier noch ein Versuch Erwähnung finden, welchen ich im Laufe der Arbeit über Phosgen mit Urethan angestellt. Urethan (7 Theile) und Phosgen (1 Theil) in Benzol gelöst, wurden im Rohr auf  $75^{\circ}$  erhitzt. Beim Oeffnen der Röhren entwich viel Salzsäure und das Benzol enthielt eine chlorfreie Substanz, welche beim Um-

<sup>1</sup> Berichte, 11, 1985 (1878).

<sup>2</sup> Berichte, 18, 1544 (1885).

krystallisiren aus Alkohol oder Chloroform langsam den Schmelzpunkt 194° erreichte. Analysen und Umwandlung in Biuret bewiesen, dass Allophansäureäthylester vorlag; selbiger kann entweder nach der Gleichung



entstanden sein, oder es hat sich intermediär Carbonydiurethan  $\text{CO}(\text{NHCOOC}_2\text{H}_5)_2$  gebildet, welches beim Umkrystallisiren zerfallen ist. Aehnliche Versuche über die Einwirkung des Phosgens auf Alanin führten zu keinem Resultate.

DAS PHOSGEN UND SEINE ABKÖMMLINGE  
NEBST EINIGEN BEITRÄGEN ZU DEREN  
KENNTNISS<sup>1</sup>

GESCHICHTLICHES

SELTEN hat sich wohl ein erbitterter Streit für die Chemie segensreicher erwiesen, als jener, welcher am Anfang unseres Jahrhunderts über die Annahme der Unzerlegbarkeit des Chlors entbrannt ist. Es war nicht nur der Fortschritt, welchen der endliche Sieg von Davy's chloristischer Theorie durch die Beseitigung mancher hemmender Hypothesen mit sich brachte: auch in materieller Hinsicht haben wir dieser Discussion viel zu verdanken. In dem Eifer, gegen ebenbürtige Gegner neue Argumente zu erlangen, ward gar manche Thatsache entdeckt, die sonst wohl lange unbekannt geblieben wäre, die uns aber heute von erster Wichtigkeit erscheint. Eines der besten Beispiele liefert das Phosgen, dessen Erkennung eine interessante Episode in jenem Streite bildete.

Als Humphry Davy<sup>2</sup> im Jahre 1811, seine Ansicht entwickelte, dass jenes Gas, welches man bisher als oxydirte Salzsäure aufgefasst, ein einfacher Körper sei, und ihm den Namen, "Chlorine" beilegte, galt unter seinen Landsleuten Dr. John Murray, der Lieblingsschüler Black's, als berufenster und eifrigster Verfechter der älteren Ansicht. Nachdem Ersterer seiner besten Argumente durch die Beweiskraft Davy'scher Experimente verlustig gegangen war, glaubte er

<sup>1</sup> *Inaugural-Dissertation* zur Erlangung der Doctorwürde von der Philosophischen Facultät der Friedrich-Wilhelms-Universität zu Berlin. 15. März, 1887. [Printed by C. Berg, Berlin, 1887.]

<sup>2</sup> H. Davy, Bakerian Lecture, *Phil. Trans.* 1811, p. 1.

seinerseits in einigen neuen Beobachtungen eine schlagende Waffe gefunden zu haben.

[2] Er hatte Kohlenoxyd und Chlor im Sonnenlichte zusammenstehen lassen, und gab nun Ammoniak hinzu, worauf eine bedeutende Volumverminderung folgte. Da nun Zusatz starker Salpetersäure zu der entstandenen Salzlösung eine Kohlensäureentwickelung hervorbrachte, folgerte Murray, dass die Lösung salzaures und kohlensaures Ammoniak enthalte, was dadurch zu erklären sei, dass, die "oxydirte Salzsäure" zerfallen und das Kohlenoxyd im freigewordenen Sauerstoff verbrannt wären. Um dieses wichtige Argument womöglich zu entkräften, wiederholte John Davy,<sup>1</sup> der seinen berühmteren Bruder unterstützte, diese Versuche und fand zu seiner Genugthuung, dass sich Chlor und Kohlenoxyd zu einem definirten Gase vereinigen, das weder Salzsäure noch Kohlendioxyd zu liefern vermag, wenn nicht anwesende Feuchtigkeit den nöthigen Wasserstoff und Sauerstoff liefert. Wenn dasselbe mit trocknem Ammoniak vermischt werde, so enthalte das entstehende Salz keine Kohlensäure, da Essigsäure solche nicht daraus austreibe. Nur beim Zusatz starker Mineralsäuren entstehe durch Wasserassimilation Kohlensäure.

Diesem Argumente war Murray nicht mehr gewachsen; jenes neue Gas aber nannte John Davy, da es unter der Einwirkung des Sonnenlichtes entsteht, Phosgen und betrachtete es als eine Säure, welche vier Aequivalente Ammoniak zur Sättigung verlange. Erst 1838 gelangte Régnault<sup>2</sup> zur Ueberzeugung, dass Ammoniak und Phosgen nicht ein einheitliches Salz bilden, sondern ein Gemisch von Salmiak und "Carbamide." Obwohl letzteres dieselbe Zusammen-

<sup>1</sup> John Davy, *Philosophical Transactions of the Royal Society*, 1812, p. 144. Nicholson's *Journal of Natural Philosophy and Chemistry* (London und Edinburgh) 30, 28. Die ganze Controverse fand in diesem Journale statt, in den Bänden 27-34.

<sup>2</sup> Régnault, *Ann. de Chim. et Phys.* 69, 180 (1838).

setzung mit Harnstoff habe, sei es doch nicht damit identisch, da noch so concentrirte Lösungen die charakteristische Fällung mit Salpetersäure nicht gäben. Er schrieb vielmehr dem "Carbamide" [3] die halbe Molekularformel des Harnstoffes zu. Natanson<sup>1</sup> jedoch, der das Carbamid sorgfältiger reinigte, erhielt ohne Mühe den salpetersauren Niederschlag der zur Identifizirung der beiden Substanzen noch fehlte.

Die Reaktion verläuft also in folgender Weise: —



Natanson schrieb Régnaults Unvermögen, den besprochenen Niederschlag zu erhalten, dem Umstande zu, dass die Gase nicht genügend getrocknet waren, weshalb ein so grosser Ueberschuss an Salmiak entstanden, dass das Carbamid nur schwer davon befreibar war. Thatsächlich ist aber die Verunreinigung auch noch darin zu suchen, dass nach Bouchardat<sup>2</sup> und Fenton<sup>3</sup> die Reaktion nie glatt verläuft, sondern als Nebenprodukte noch Guanidin-, Cyanursäure und Melanurensäure auftreten. An besonderer Bedeutung gewann aber Régnaults Reaktion durch Hofmann,<sup>4</sup> der am Anilin zeigte, dass sie auch auf die Amine ausdehnbar sei.

Noch vor Régnault hat Dumas sich mit dem Phosgengas beschäftigt, und zwar ist es seine wichtige Reaktion mit den Alkoholen, welche er 1833<sup>5</sup> in voller Klarheit auseinandersetzte. Das Warum und das Wie entnehme ich der schönen Schilderung, welche mein verehrter Lehrer von Dumas Leben und Wirken entworfen hat.<sup>6</sup>

"Der Analyse nach liess sich der Zucker als eine Ver-

<sup>1</sup> Natanson, *Liebigs Annalen* [hereafter designated as *Annalen*] **98**, 287 (1856).

<sup>2</sup> Bouchardat, *Comptes Rendus*, **69**, 962 (1869).

<sup>3</sup> Fenton, *J. Chem. Soc.* **35**, 793 (1879). Der Auszug im Jahresbericht 1879, ist darin unrichtig, dass es F. Bouchardats Erfahrungen nicht widerspricht: das Vorhandensein von Guanidin bestätigt er; nach den andern Nebenprodukten hat er nicht gesucht.

<sup>4</sup> Hofmann, *Annalen*, **57**, 267 (1846). <sup>5</sup> Dumas, *Annalen*, **10**, 277 (1834).

<sup>6</sup> Hofmann, *Nekrolog auf Dumas*, *Ber. deutsch. ch. Ges.* **17** (1884), Ref. 662 ff.

bindung von Alkohol und Kohlensäure auffassen, und diese [4] Auffassung schien in der Spaltung des Zuckers durch den Gährungsprozess eine Bestätigung zu finden. Allerdings war es nicht gelungen, durch direkte Vereinigung von Alkohol und Kohlensäure Zucker zu erzeugen. Allein konnte man hoffen, dass sich diese Vereinigung würde bewerkstelligen lassen, wenn man dem Alkohol die Kohlensäure *in condicione nascendi* böte. Diese Betrachtung veranlasste Dumas, die Einwirkung des Phosgengases auf den Alkohol zu studiren.

“Er hoffte eine Verbindung zu erhalten, welche, mit Wasser behandelt, Salzsäure und Kohlensäure liefern würde und, wenn letztere mit dem Alkohol in Verbindung blieb, Zucker erzeugen konnte. Diese Hoffnung ist allerdings unerfüllt geblieben, aber der Versuch hat zur Entdeckung des Chlorkohlensäure-Aethers geführt, welcher unter dem Einflusse des Ammoniaks in Urethan oder Carbaminsäure-Aether übergeht. Die Zusammensetzung, welche Dumas für diese beiden typischen Verbindungen feststellte, ist die noch heute anerkannte; aber wie viele Entdeckungen sind seitdem von den Chemikern auf dem von ihm erschlossenen Gebiete gemacht worden, und welche Ernten verspricht auch heute noch die Bebauung derselben, zumal seit die neueste Schwenkung der Farbenindustrie das ehedem nur schwierig zugängliche Phosgengas verflüssigt der Forschung in beliebiger Menge zur Verfügung stellt.”

Was nun, seit jenen frühen Tagen, zur Kenntniss des Phosgengs und seiner Abkömmlinge beigetragen worden, und welche Ansichten die Nachfolger Davys, Régnaults und Dumas geleitet, das hoffe ich im Folgenden geordnet darzuthun.

#### DARSTELLUNG

Zur Darstellung des Phosgengs im Grossen dient noch immer die Methode Davys, gleiche Volume Kohlenoxyd und

Chlor den Sonnenstrahlen auszusetzen. Die Vereinigung erfolgt rasch, und kann man, wenn man mit grossen Gefässen [5] arbeitet, das Gas durch Abkühlung verflüssigen und so auffangen, bei kleineren Quantitäten leitet man das Gas in Lösungsmittel ein. Um die grossen Glasgefässe und die Nothwendigkeit der Belichtung zu vermeiden, hat man auch häufig Hofmann's Darstellungsmethode<sup>1</sup> vorgezogen, bei der man Kohlenoxyd zur Chlorirung über siedendes Antimonpentachlorid leitet. Paternò<sup>2</sup> will die directe Vereinigung des Kohlenoxyds mit Chlor dadurch bewirken dass er die Gase über Knochenkohle leitet. Es giebt noch viele Vorschläge, das Phosgen durch Oxydation von Tetrachlorkohlenstoff<sup>3</sup> oder Chloroform<sup>4</sup>, oder durch Wechselwirkung derselben mit Kohlenoxyd<sup>5</sup> darzustellen. Da aber die Entstehung lästiger Nebenprodukte unvermeidlich ist, und auch die angewandten Substanzen häufig von erschwerender Beschaffenheit sind, hat sich keines dieser Verfahren einzürgern können.

Während diese Methoden alle eine Synthese des Phosgens aus seinen Bestandtheilen bedeuten, sind einige noch aus theoretischen Gründen bemerkenswerth, da sie in einem Abscheiden des Phosgens aus komplizirteren Verbindungen bestehen und gerade deshalb neuerdings anscheinend wieder hervorgeholt werden.

Schon Berzelius<sup>6</sup> hatte entdeckt, dass durch Einwirkung feuchten Chlorgases auf Schwefelkohlenstoff eine Substanz entsteht, die mit Schwefelsäure behandelt Chlorkohlenoxyd

<sup>1</sup> Hofmann, *Annalen*, **70**, 139 (1849).

<sup>2</sup> Paternò, *Gazzeta Chimica Italiana*, **8**, 233 (1878).

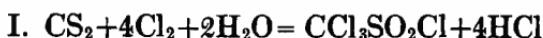
<sup>3</sup> Gustavson, *Zeitschrift für Chem.* 1871, 615. Schützenberger, *Compt. Rend.* **66**, 747 (1868).

<sup>4</sup> Dewar und Cranston, *Chem. News*, **20**, 174 (1869). Emmerling und Lengyel, *Berichte*, **2**, 547 (1869).

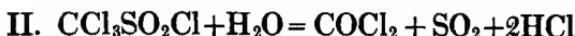
<sup>5</sup> Schützenberger, *Compt. Rend.* **66**, 747 (1868).

<sup>6</sup> Berzelius und Marçet, *Gilbert's Annalen*, **48**, 161.

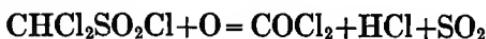
abspaltet. Kolbe<sup>1</sup> verdanken wir die Bestätigung und [6] nähere Erklärung dieser Reaktion, die nach den heutigen Formeln folgendermassen verläuft: —



Trichlormethyl  
sulfonsäurechlorid



Noch leichter lässt sich das Phosgen aus Dichlormethyl-sulfonsäurechlorid abspalten, indem dasselbe sich an der Luft oxydirt.



Kolbe fand auch dass das trockene Natriumsalz der Tri-chloressigsäure beim Erhitzen Phosgen liefert



Perchlorameisensäuremethylester lässt sich als Polymer des Chlorkohlenoxids auffassen und zerfällt auch beim Durchstreichen auf 340–350° erhitzter Röhren in dasselbe<sup>2</sup>



Auch verhält sich der Ester Reagentien gegenüber dem Phosgen analog. Ebenso scheint Schützenbergers<sup>3</sup> Carbonyl-chloroplatinit  $\text{PtCl}_2 \cdot \text{CO}$  mit Leichtigkeit in Platin und Phosgen zu zerfallen, und könnte wohl manchmal da nützlich sein, wo ein fester Aggregatzustand der Reagentien wünschenswerth erschiene.

#### BESCHREIBUNG

Wir kennen das Phosgen als ein farbloses erstickend riechendes und die Schleimhäute heftig angreifendes Gas, welches bei gewöhnlichen Drucke erst unter 0° C. condensirt

<sup>1</sup> Kolbe, *Annalen*, 54, 148 (1845).

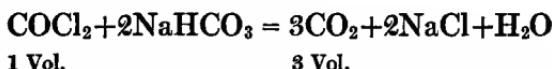
<sup>2</sup> Cahours, *Ann. de Chim. et Phys.* [3], 19, 352 (1847).

<sup>3</sup> Schützenberger, *Jahresbericht*, 1870, 381.

wird, obwohl sein Siedepunkt bei  $8.2^{\circ}$  liegt.<sup>1</sup> Die Flüssigkeit besitzt bei  $0^{\circ}$  das specifische Gewichte 1.432.

[7] Es ist in Aether, Chloroform, den flüssigen Kohlenwasserstoffen, Schwefelkohlenstoff und Chlorschwefel, sowie in den flüssigen Metallchloriden, sehr leicht löslich. Nach Berthelots Beobachtung<sup>2</sup> nimmt das Benzol bei sinkender Temperatur immer grössere Mengen des Phosgens auf, bis beim Gefrierpunkte des Benzols das sich verflüssigende Phosgen seinerseits als Lösungsmittel fungirt. Da diese Löslichkeit von keiner chemischen Wirkung bedingt ist und sich die beiden Substanzen unter den meisten Umständen indifferent zu einander verhalten, wird das Phosgen vielfach in Benzollösung angewandt, besonders auch wegen der Möglichkeit genauen Abwägens.

Von Wasser wird Phosgen in der Kälte langsam, in der Wärme rasch zerlegt, wobei sich Salzsäure und Kohlendioxid bilden und viel Wärme frei wird.<sup>3</sup> Zur quantitativen gasometrischen Bestimmung des Phosgens hat Berthelot<sup>4</sup> eine sehr charakteristische Methode ersonnen, welche auf der Verdreifachung seines Volums beim Einbringen feuchten Natriumbicarbonats beruht



Da das Phosgengas so leicht aus Kohlenoxyd und Chlor entsteht, wäre es zu erwarten, dass ohne allzugrosse Schwierigkeit auch Jod, Brom und Cyan zum Vereinigen mit Kohlenoxid zu bringen wären. Im Gegentheil lässt sich Bromkohlenoxyd nur schwierig durch Oxydation des Bromoforms

<sup>1</sup> Emmerling und Lengyel, *Annalen*, Suppl. 7, 105 (1868–1870).

<sup>2</sup> Berthelot, *Annalen*, 156, 228 (1870).

<sup>3</sup> Nach Berthelot (*Annales* [5] 7, 129) (1879) entstehen bei der Reaktion  $\text{COCl}_2 + \text{H}_2\text{O} + \text{Ag} = \text{CO}_2\text{Ag} + \text{HClAg}, +65600 \text{ cal.}$ ; nach Thomsen (*Berichte*, 16, 2619) (1873) 57970 cal.

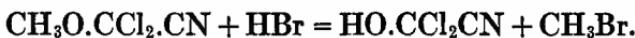
<sup>4</sup> Berthelot, *Annalen*, 156, 228.

erhalten<sup>1</sup> und ist eigentlich noch nie ganz rein dargestellt und beschrieben worden.

Das Jodphosgen hat man überhaupt noch nicht zu Stande gebracht.<sup>2</sup> Auf das Cyankohlenoxyd ist schon vielfach [8] gefahndet worden, da es nicht nur wegen seiner Analogie mit dem Chlorkohlenoxyd, sondern auch als Nitril einer zweibasischen Ketonsäure Interesse geboten hätte. Es sind wohl in der Litteratur verschiedene Notizen zu finden, welche über fehlgeschlagene Versuche berichten und neue ankündigen;<sup>3</sup> da jedoch über die letzteren nie berichtet wurde, kann man wohl annehmen, dass auch sie resultatlos verlaufen sind.

Dagegen ist neuerdings die Existenzfähigkeit des Chlorcyan-kohlenoxyds  $\text{OCCl}_2\text{CN}$ , als eines dem Phosgen sehr ähnlichen

Gases ausser Frage gestellt. Indem Bauer<sup>4</sup> im Laufe einer Untersuchung chlorirter Nitrile, Bromwasserstoffgas auf Dichlormethoxyacetonitril einwirken liess, erhielt er neben Brommethyl nur noch einen festen Körper, welcher sich beim Erhitzen unter theilweiser Verkohlung in ein schweres scharfriechendes Gas verwandelte, dessen Zersetzungspunkt es mehr als wahrscheinlich machte, dass Chlorcyan-kohlenoxyd vorliege. Die Reaktion hätte mithin den Verlauf genommen



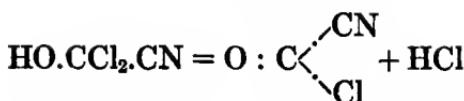
Bauer vermutet dass dieser Körper unbeständig sei und sofort die Zersetzung in Salzsäure und Chlorcyan-kohlenoxyd erleide.

<sup>1</sup> Emmerling, *Berichte*, **13**, 873 (1880).

<sup>2</sup> Cowardins, *Chem. News*, **48**, 97 (1883).

<sup>3</sup> So Carstanjen und Schertel, *Journ. prakt. Chem. [2]*, **4**, 49 (1871). Gintl, *ibid.*, 362.

<sup>4</sup> Bauer, *Annalen*, **229**, 187 (1885).



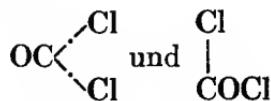
Dass das Phosgen vielfach als Analogon des Kohlendioxids und Kohlenoxysulfids zu betrachten wäre, erhellt sowohl aus seiner Bildungsweise, als aus den Thatsachen dass manche [9] seiner Derivate mit derselben Leichtigkeit aus letzterem erhalten werden können, während es sich selber bei vielen Reaktionen in ersteres umwandelt. Dagegen ist schon früh beobachtet worden, dass in Fällen wo man seine beiden Chloratome *successive* ersetzen wollte, das zweite Chloratom sich viel beständiger verhielt als das erste. Durch blosses Zusammenbringen von Chlorkohlenoxyd und Alkohol wird ein Chloratom ausgewechselt und es entsteht der Ester der Chlorameisensäure. Dagegen ist erhöhte Temperatur, längeres Stehen oder dergleichen nötig, um auch das zweite Chloratom zum Austritt zu bewegen. Um dies zu betonen, fasst man das Phosgen gerne als Chlorameisensäurechlorid auf: es gab sogar eine Zeitlang ernstliche Meinungsunterschiede, da Manche sich die beiden Chloratome in verschiedener Weise im Molekül functionirend dachten. Schreiner<sup>1</sup> glaubte gar diese Verschiedenheit in den Derivaten wieder finden zu können und behauptete, dass, wenn er aus Phosgen und Methylalkohol bereiteten Chlorameisensäure-Methylester mit Natrium-Aethylat behandelte, das Produkt verschieden sei von dem gemischten Ester aus Chlorameisensäure-Aethylester und Natrium-Methylat. Eine gründlichere Untersuchung von Roesse<sup>2</sup> erwies jedoch diese Idee als nichtig.

Die heutige Auffassung der Zustände in Molekül macht aber auch ein Disput über diese Frage inhaltslos. Es würde

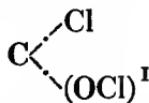
<sup>1</sup> Schreiner, *Journ. prakt. Chem.* [2], **22**, 353 (1880).

<sup>2</sup> Roesse, *Annalen*, **205**, 227 (1880).

von gedankenloser Gewöhnung an das rein Aeusserliche der graphischen Formeln zeugen, müssten wir uns immer erst klar machen, dass in den Säurechloriden auch das Chlor direkt mit dem Kohlenstoff verbunden ist, so dass kein Unterschied besteht zwischen



[10] Ernstlich eine Constitution anzunehmen



würde uns zum zweiwerthigen Kohlenstoff führen und wäre durch die Constitution von keinem der Derivate zu begründen. Bleiben wir also bei der herkömmlichen Formel des Phosgens und denken wir uns keine verschiedene Bindekraft des Kohlenoxyds für die beiden Chloratome: alsdann können wir getrost die Ursache der grösseren Beständigkeit der Chlorameisensäureester darin suchen, dass, nachdem beim ersten Zusammenstoss der Moleküle ein Chloratom durch die Alkoxyl-Gruppe ersetzt worden, nunmehr ein derartiger Gleichgewichtszustand zwischen den positiven und negativen Principien im Molekül eingetreten ist, wie wir ihm sonst häufig begegnen. Denkt man sich z. B. die Schwefelsäure etwa unsymmetrisch constituit, weil Benzolsulfonsäure eine beständige Verbindung ist, und nicht bei der Darstellung in Sulfonylbenzid übergeht?

#### ABKÖMMLINGE

Die Einwirkung des Phosgens auf anorganische Substanzen bietet kein Interesse: es wirkt entweder unter direkter Abgabe seines Chlors oder unter Austausch desselben gegen

Sauerstoff. Auch unter den kohlenstoffhaltigen Körpern giebt es manche, auf die es genau wie Phosphorpentachlorid reagirt. So fand Kempf<sup>1</sup> dass Benzaldehyd in Benzalchlorid, Aceton in Dichloraceton, Essigsäure in Acetylchlorid verwandelt wird. Neuerdings soll aus letzterer Reaktion mit gutem Erfolge die technische Anwendung gezogen werden, dass man, behufs Bildung der Säureanhydride, Phosgengas in die erhitzen Säuren oder deren Salze leitet.<sup>2</sup>

[11]



Die Reaktion zwischen Phosgen und Aldehyd war Gegenstand eines merkwürdigen Irrthums, welcher auf die chemische Theorie einigen Einfluss haben musste und dessen Beseitigung wir Kekulé und Zincke verdanken. 1858 beschrieb Harnitz-Harnitzky<sup>3</sup> einen Körper, "Chloraceten" durch Einwirkung von Chlorkohlenoxyd auf Aldehyddampf entstanden. Daselbe habe einen konstanten Siedepunkt, sei bei gewöhnlicher Temperatur flüssig, bei 0° krystallinisch fest. Analysen und Dampfdichte Bestimmung ergaben die Formel C<sub>2</sub>H<sub>3</sub>Cl, welche jedoch auch dem Vinylchlorid zukomme, von dem das Chloraceten sehr verschieden sei. Da die Constitution des Vinylchlorids ohne Zweifel CH<sub>2</sub>=CHCl ist, musste das

II

Isomer, aus Aldehyd entstanden, CH<sub>3</sub>-C-Cl sein. Das zweiwerthige Kohlenstoffatom erweckte Interesse. Friedel,<sup>4</sup> Kraut,<sup>5</sup> Stacewitz<sup>6</sup> stellten den Körper nach Harnitz-Harnitzkys Angaben dar und machten Derivate welche die

<sup>1</sup> Kempf, *Journ. prakt. Chem.* [2], 1, 402 (1870).

<sup>2</sup> Hentschel, *Berichte*, 17, 1284 (1884).

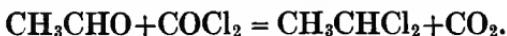
<sup>3</sup> Harnitz-Harnitzky, *Annalen*, 111, 192 (1859).

<sup>4</sup> Friedel, *Compt. Rend.* 60, 930 (1865). *Ann. chim. et phys.* [4], 16, 403 (1869).

<sup>5</sup> Kraut, *Annalen*, 147, 107 (1868).

<sup>6</sup> Stacewitz, *Zeitschrift f. Chemie* (1869), 321.

Constitution erhärten sollten. Indem sie aber Harnitz-Harnitzkys Beschreibung des "Chloracetens" bestätigt fanden, zweifelten sie auch nicht an der Richtigkeit seiner Analysen und Constitutionserklärung. Kekulé und Zincke<sup>1</sup> theilten jedoch dieses Vertrauen nicht und ihre eingehende Untersuchung ergab die Nichtexistenz des "Chloracetens." Sie fanden dass die hierfür gehaltene Substanz ein Gemisch von Aldehyd und Phosgen sei, ohne bestimmte Zusammensetzung und ohne Beständigkeit. Das Phosgen begünstige die Entstehung von Paraldehyd, habe aber sonst keine Wirkung. Die aus "Chloraceten" entstandenen Derivate leiteten sie theils selber vom unveränderten Aldehyd her, theils ist dies seither von Andern [12] geschehen. Allerdings wäre zu erwarten gewesen, dass Aldehyd nach Analogie des Benzaldehyds, in Aethylidenchlorid übergegangen wäre



Dies glaubt auch Eckenroth<sup>2</sup> neuerdings beobachtet zu haben: da jedoch die diesbezügliche Angabe nur in einer kurzen Erwähnung der Thatsache besteht, lässt es sich noch nicht erklären, warum das Aethylidenchlorid der genauen Forschung Kekulé und Zinckes entgangen sein soll.

Wenden wir uns nun zu denjenigen Synthesen, in denen mittels der Carbonylgruppe ein wahrer Aufbau stattfindet, so ist die Anzahl der Fälle einer direkten Anlagerung an Kohlenstoff in der Fettreihe etwas beschränkt. Bis vor Kurzem hatten wir nur eine unglückliche Angabe Harnitz-Harnitzkys<sup>3</sup> dass Kohlenwasserstoffe und Phosgen Säurechloride lieferten, welcher Berthelots und dessen Schüler<sup>4</sup>

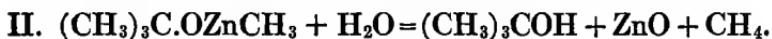
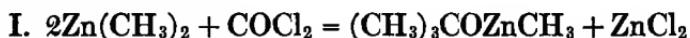
<sup>1</sup> Kekulé und Zincke, *Annalen*, **162**, 125 (1872).

<sup>2</sup> Eckenroth, *Berichte*, **18**, 518 (1885). Anmerkung.

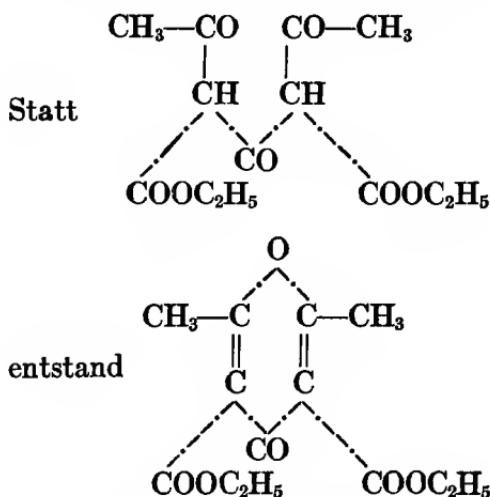
<sup>3</sup> Harnitz-Harnitzky, *Compt. Rend.* **58**, 748 (1864). *Ann.* **136**, 121 (1865). *Compt. Rend.* **60**, 923 (1865).

<sup>4</sup> Berthelot, *Annalen*, **156**, 216 (1870). De Clermont et Fontaine, *Ibid.* **226**. *Bull. Soc. Chim. n. s.* **13**, 9 (1870).

genauere Untersuchungen alle Glaubwürdigkeit geraubt hatten; sodann eine Beobachtung Butlerows,<sup>1</sup> dass Zinkmethyl mit Phosgen in Sonnenlichte eine krystallinische Verbindung abgibt, welche mit Wasser in Trimethylcarbinol übergeht. Nach andern von Butlerow ausgeführten Reaktionen dürfte man sich wohl den Vorgang in folgender Weise vorstellen: —



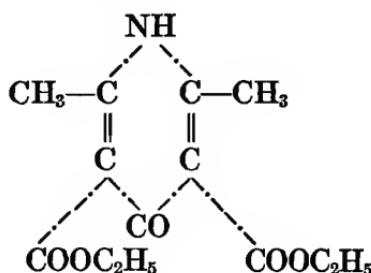
Nachdem, man mehrfach vergebens versucht hatte, Chlor-kohlenoxyd,<sup>2</sup> analog anderen Säurechloriden, auf Natrium-acetessigester einwirken zu lassen, haben im vorigen Jahre Conrad und Guthzeit<sup>2</sup> unter Anwendung des Kupfersalzes des [13] Acetessigesters ein sehr günstiges Resultat erzielt. Das Produkt der Einwirkung ist jedoch nicht, wie erwartet, ein Carboxyldiacetessigester (Diacetylacetondicarbon-säureester) sondern dessen Dehydroverbindung.



<sup>1</sup> Butlerow, *Berichte*, **3**, 426 (1870).

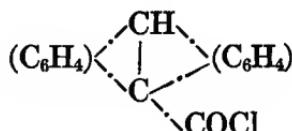
<sup>2</sup> Conrad und Guthzeit, *Berichte*, **19**, 190 (1886).

Es genügt, diesen Körper mit Ammoniak zu behandeln, um ein Pyridinderivat zu erhalten, den Dimethyloxypyridindicarbonsäure-Aethylester.



Die Anwendung eines primären Amines statt des Ammoniaks führt zum entsprechenden Substitutionsprodukt dieses eigenartigen Körpers. Jedenfalls dürfte diese Reaktion des Phosgens noch bedeutsamer Variirung fähig sein.

In der aromatischen Reihe ist eine unmittelbare Einwirkung des Phosgens auf einen Kohlenwasserstoff nur von [14] Graebe und Liebermann<sup>1</sup> beobachtet worden. Es entsteht bei 200° ein Anthracencarbonsäurechlorid. Behla<sup>2</sup> hat dies als γ-Derivat erkannt



und auch gefunden, dass bei höheren Temperaturen γγ-Chloranthracencarbonsäurechlorid und γγ-Dichloranthracen entstehen.

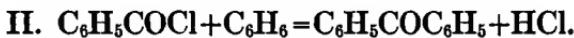
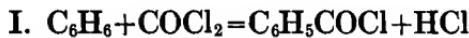
Friedel, Ador und Crafts<sup>3</sup> wussten durch Vermittelung des Aluminiumchlorids einen sofortigen Eintritt des Carbonyls in den Benzolkern zu bewerkstelligen, und erhielten

<sup>1</sup> Graebe und Liebermann, *Berichte*, **2**, 678 (1869).

<sup>2</sup> Behla, *Berichte*, **18**, 3169 (1885).

<sup>3</sup> Friedel, Ador und Crafts, *Berichte*, **10**, 1854 (1877).

je nach der Dauer der Einwirkung Benzoylchlorid oder Benzophenon,



Dies Verfahren ist allgemein und ist nicht nur bei den Homologen des Benzols, sondern auch in der Thiophenreihe angewandt worden.

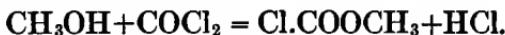
Drittens liess Wurtz<sup>1</sup> Natrium auf Brombenzol und Phosgen einwirken.



Wenn diese Reaktion auch typisch ist, so hat sie doch in dieser Form nur einmal Anwendung gefunden; man zieht vor, das Phosgen durch den verwandten Chlorameisensäure-Ester zu ersetzen.

Ein vierter Beispiel Synthesen dieser Art wird sich später so viel besser besprechen lassen, dass ich nun zur Wirkung des Chlorkohlenoxyds auf hydroxylhaltige Verbindungen übergehe.

[15] Wie schon angedeutet worden ist, entsteht beim Einleiten von Phosgen in einen Alkohol immer der Chlorameisensäureester (Chlorkohlensäureester): wie zum Beispiel bei Anwendung des Methylalkohols



Eine Ausnahme bildet bis jetzt nur das Glycol, dessen zwei Hydroxylgruppen zugleich in Reaktion tretend, zum normalen Carbonat führen.<sup>2</sup> Aus einem Chlorameisensäure-ester entsteht der neutrale Kohlensäure-Ester erst beim längeren Stehen oder Erhitzen mit dem Alkohol oder durch Einwirkung des Natriumalkoholats. Durch Anwendung

<sup>1</sup> Wurtz, *Comptes Rendus*, **68**, 1298 (1869).

<sup>2</sup> Nemirovsky, *Journ. prakt. Chem.* **28**, 439 (1883).

anderer als des ursprünglichen Alkohols kann man zu den mannigfältigsten gemischten Estern gelangen. Auch greift Wasser die Chlorameisensäureester an, unter Bildung von sauren kohlensauren Estern, welche Alkalien zu verbinden vermögen. Ferner lässt sich das Chloratom im Chlorameisen-säureester durch einen Ammoniak- oder Amin-Rest ersetzen. Dumas, welcher zuerst die Reaktion



ausführte,<sup>1</sup> erkannte sofort, dass der neue Körper zum Harn-stoff in derselben Beziehung stehe, wie Oxamaethan zum Oxamid: er wählte deshalb den Namen Urethan. Es ist dies der Ester der hypothetischen Carbaminsäure. Wenn Amine in dieser Reaktion das Ammoniak vertreten, entstehen natür-lich Ester substituirter Carbaminsäuren.

Es kann als Regel gelten, dass jeder Körper welcher mit Phosgen reagirt, auch mit dem Chlorameisensäureester eine entsprechende Verbindung geben muss. Die leichtere Hand-habung des letzteren, als einer höher siedenden, geruchlosen und unschädlichen Flüssigkeit, hat ihm auch zu einer grösseren Beliebtheit verholfen, so dass die Anzahl seiner Derivate fast unabsehbar ist. Für die Wurtz'sche und Friedel und Crafts'-sche Reaktionen mit Kohlenwasserstoffen, für die [16] Darstellung mannigfaltiger Aminsäuren und Harnsäurederiva-ten ist diese Substanz unschätzbar.

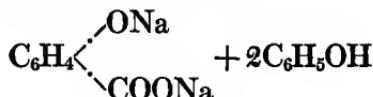
Phenole verbinden sich ebenfalls mit Phosgen zu Chlorameisensäureestern;<sup>2</sup> es giebt aber das gewöhnliche Phenol schon sofort etwas Phenylcarbonat und aus Resorcin lässt sich auf diese Weise nur Resorcincarbonat darstellen.<sup>3</sup> Sehr auffallend ist es, dass Chlorkohlenoxyd durch auf 200° erhitztes Phenolnatrium geleitet, auch Salicylsäure liefern

<sup>1</sup> Dumas, *Ann. chim. et phys.* [2], **54**, 226 (1833).

<sup>2</sup> Kempf, *Journ. prakt. Chem.* [2], **1**, 402 (1870).

<sup>3</sup> Birnbaum und Lurie, *Berichte*, **14**, 1754 (1881).

kann.<sup>1</sup> Zur Erklärung der Reaktion muss bemerkt werden, dass ein Ueberschuss an Natriumhydroxyd nothwendig ist und dass allerdings das meiste Phenol unverändert abdestillirt. Da fernerhin auch durch Zusammenschmelzen von Phenylcarbonat und Phenolnatrium Salicylsäure entstehen soll, kann man sich die Reaktion in zwei Stadien zerfallend denken, wovon das erstere die Bildung des Phenylcarbonats bewirkt. Darauf folgt



Salomon,<sup>2</sup> und neuerdings Schöne,<sup>3</sup> haben gezeigt dass sich die Merkaptane in ihrem Verhalten gegenüber Phosgen und Chlorameisensäureester in keiner Weise von den Alkoholen unterscheiden. Auch hier ist es bei der Darstellung gemischter Ester gleichgültig, ob man das Phosgen direkt auf das Merkaptan einwirken lässt und Natriumalkoholat zufügt, oder ob man mit Chlorameisensäureester auf das Natriummerkaptid wirkt.

An Zahl und Interesse die wichtigsten sind die stickstoffhaltigen Derivate des Phosgens. Wir haben schon gesehen [17] wie Chlorkohlenoxid mit Ammoniak zusammengebracht Harnstoff liefert; so entsteht auch mit Anilin<sup>4</sup> in äusserst heftiger Reaktion das Carbanilid, Diphenylharnstoff, und aus jedem primären Amine der entsprechende, symmetrisch zweifach-substituirte Harnstoff.

Aus vielen Beispielen hat Michler<sup>5</sup> dagegen gezeigt, dass

<sup>1</sup> Deutsche Patente 29929, 30172, 24151, siehe *Berichte*, 18, Ref. 12, 40, 90 (1885).

<sup>2</sup> Salomon, *Journ. prakt. Chem.* [2], 6, 433 ff. (1872). 7, 254 (1873).

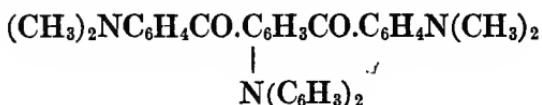
<sup>3</sup> Schöne, *Journ. prakt. Chem.* [2], 30, 416 (1884).

<sup>4</sup> Hofmann, *Annalen*, 57, 267 (1846).

<sup>5</sup> Michler et alii, *Berichte*, 12, 1162, 1166 (1879). 8, 1665 (1875). 9, 396 (1876). Willm und Girard, *Berichte*, 9, 449 (1876).

sich sekundäre Amine insofern wie Alkohole verhalten, als sie im Phosgen vorerst nur ein Chloratom ersetzen. So erhält er aus Diäthylamin  $(C_2H_5)_2NCOCl$  welches er Diäthylharnstoffchlorid nennt, obwohl die Bezeichnung als Diäthylcarbaminsäurechlorid verständlicher wäre. Das Chlor kann durch Erhitzen mit frischen Mengen desselben oder eines andern Amines ersetzt werden. Auch kommt man mittels Natriumalkoholate wieder zu Urethanen, in diesem Falle Estern der zweifach substituirten Carbaminsäuren.

Tertiäre Basen der rein aliphatischen Reihen scheinen dem Phosgen keinen Angriffspunkt zu bieten: dagegen tritt bei den dialkylierten Anilinen die Carbonylgruppe in den Benzolrest ein, und zwar in die Parastellung zur Amidogruppe. Dimethylanilin<sup>1</sup> wird mit Phosgen schon bei niederer Temperatur zu Dimethylparaamidobenzoylchlorid. Dieses greift bei höherer Temperatur wiederum das überschüssige Dimethylanilin an, unter Bildung des Hexamethyltriamido-benzoylbenzols.<sup>2</sup>



Man dürfte erwarten auch das tetraalkylierte Diparaamidobenzophenon unter den Reaktionsprodukten zu finden. Dies ist allerdings dann der Fall, wenn das hierzu berechnete Mengenverhältniss eingehalten wird. Im allgemeinen fand aber Michler dasselbe nicht, an seiner Statt jedoch einen [18] blauen oder violetten Farbstoff<sup>3</sup> dessen sich seit 1885 die Technik bemächtigt hat und von dem Hofmann<sup>4</sup> bewiesen hat, dass er, bei angewandten Dimethylanilin das reine Hexamethylpararosanilin repräsentire. Die Reaktion geht im

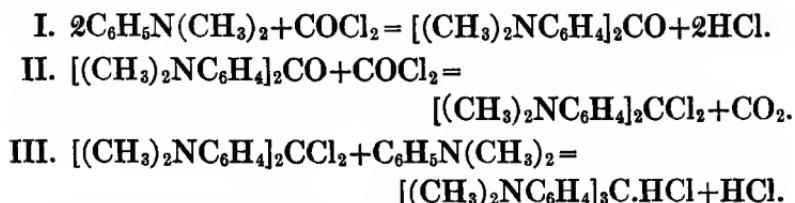
<sup>1</sup> Michler, *Berichte*, **9**, 400 (1876).

<sup>2</sup> Michler und Dupertius, *Berichte*, **9**, 1899 (1876).

<sup>3</sup> Michler, *Berichte*, **9**, 716 (1876).

<sup>4</sup> Hofmann, *Berichte*, **18**, 770 (1885).

Autoklaven vor sich, und Hofmann fand die folgenden Gleichungen für die wahrscheinlichsten.



In Gegenwart von Aluminiumchlorid lässt sich derselbe Farbstoff gewinnen, wenn Chlorameisensäureester das Phosgen vertritt;<sup>1</sup> oder aber, man kann gleich fertiges Tetramethyldiamidobenzophenon mit tertiären Anilin einschliessen.<sup>2</sup> Es braucht in beiden Fällen nur die zweite Gleichung in der Weise modifizirt werden, dass das Aluminiumchlorid das Phosgen als Chlorüberträger vertritt. Bemerkenswerth ist noch der Umstand, dass man auch aus Perchlormeisen-säuremethylester den Farbstoff gewinnen will:<sup>3</sup> es ist dies eine praktische Erkennung der Thatsache, dass dieser Ester mit Phosgen polymer und für derartige Reaktionen identisch ist.

Für die eigenthümliche Stellung der Imidgruppe im Pyrrol ist charakterisch, dass sich dasselbe dem Phosgen gegenüber fast eben so gut wie ein Kohlenwasserstoff als wie ein sekundäres Amin gebahrt. Ciamician und Magnaghi<sup>4</sup> haben nämlich gefunden, das sich aus dem Pyrrolkalium neben dem zu erwartenden Harnstoffe (Carbonylpyrrol)



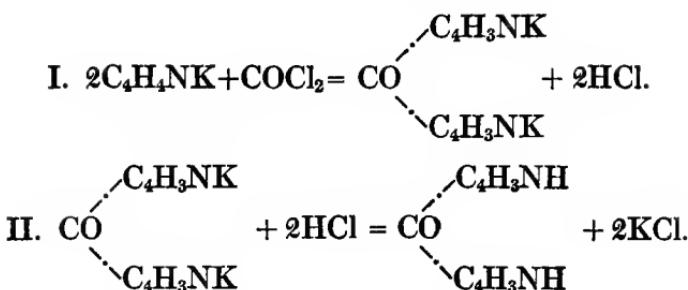
[19] auch das Dipyrrylketon bildet, eine Reaktion die Räthselhaftes bietet, aber doch nur in folgender Weise gedeutet werden kann:—

<sup>1</sup> Deutsches Patent 29962, *s. Berichte*, 18, Ref. 40 (1885).

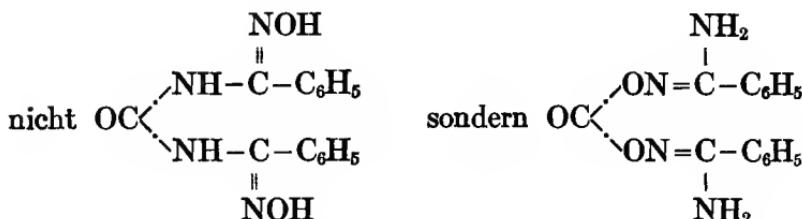
<sup>2</sup> D. R. P. 34463. *Berichte*, 19, Ref. 226 (1886).

<sup>3</sup> D. R. P. 34607. *Berichte*, 19, Ref. 278 (1886).

<sup>4</sup> Ciamician und Magnaghi, *Berichte*, 18, 414 (1885).



Noch schwieriger möchte die Erklärung zu finden sein, warum bei den Amidoximen das Phosgen die primäre Aminogruppe nicht berühren soll, während es sofort die Nitrolgruppe angreift. So entsteht z. B. nach Falck<sup>1</sup> beim Benzenylamidoxim



Bis jetzt weiss man nur, dass sich diese Anomalie auch bei andern Reaktionen der Amidoxime wiederfindet.<sup>2</sup> Jedenfalls kann es sonst als Regel gelten, dass da, wo die primäre Aminogruppe in complexeren Körpern vorkommt, sie immer dem Phosgen den gewohnten Angriffspunkt bietet.

Augenscheinlich in der Erwartung, dass die Phosphine sich dem Phosgen gegenüber ebenso verhalten würden wie die Amine, haben Michaelis und Dittler<sup>2</sup> mit Phenylphosphin den Versuch angestellt. Es zeigte sich jedoch, dass Phosphor für das Chlor die stärkere Anziehungskraft habe

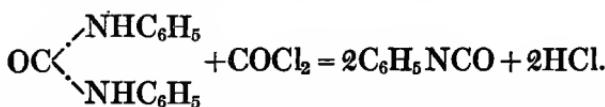


<sup>1</sup> Falck, *Berichte*, **18**, 2471 (1885).

<sup>2</sup> Michaelis und Dittler, *Berichte*, **12**, 339 (1879).

Da die Carbonylgruppe nur selten mit fünfwerthigem Stickstoff verbunden auftritt, steht zu erwarten dass, wenn [20] überhaupt das Carbonylchlorid auf den Aminen entsprechende Ammoniumsalze einwirkt, dies nur bei hohen Temperaturen und unter Dissociation des Salzes geschehen werde. Dass in der That eine Einwirkung unter solchen Umständen stattfinden kann, hat Hentschel in der Verfolgung eines glücklichen Gedankens bewiesen.

Hofmann, der Entdecker des Phenylisocyanats, sogenannten Carbanils, lehrte dasselbe auf zweierlei Weisen darstellen: einerseits durch trockene Destillation des Carbanilids oder Oxalyldiphenylguanidins,<sup>1</sup> andererseits durch Erhitzen des Phenylcarbaminsäure-Aethylesters mit Phosphorsäureanhydrid.<sup>2</sup> Letztere Weise, die allein praktisch ausführbare, war dennoch mühselig und kostspielig, so dass das Carbanil nur in kleinen Mengen hergestellt worden war. Hentschel's<sup>3</sup> erfolgreicher Gedanke bestand nun darin, dass er Phosgen-gas über geschmolzenes Carbanlid leitete —



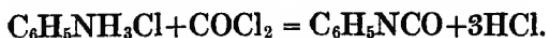
Da aber das Carbanlid selbst aus Anilin und Phosgen entsteht, war es nur noch ein Schritt die Darstellung des Carbanils direkt aus Anilin und Phosgen anzustreben. Um jedoch zu verhüten, dass bei der Destillation Anilin mit dem Phenylcyanat übergehe und dasselbe in der Vorlage in Carbanlid verwandle, wandte er salzaures Anilin an, durch welches er bei 200° Phosgen leitete. Dies Verfahren ist so vortheilhaft, dass es eine fabrikmässige Darstellung des Carbanils ermöglicht hat, und auch zur Kenntniss vieler Isocya-

<sup>1</sup> Hofmann, *Annalen*, **73**, 9 (1850). **74**, 33 (1850).

<sup>2</sup> Hofmann, *Berichte*, **3**, 655 (1870).

<sup>3</sup> Hentschel, *Berichte*, **17**, 1284 (1884).

nate führte, die nun aus den entsprechenden Aminen in einer Operation erreicht werden konnten. Die Gleichung zeigt, dass in der That eine Dissociation des Salzes in der Reaktion begriffen ist.



[21] Man wird 'dabei an Bouchardat's Erfahrung erinnert,<sup>1</sup> der ja, beim Einleiten von Ammoniakgas in Phosgen, neben Harnstoff und Guanidin auch Cyanursäure und Melanuronsäure fand. Die letzteren beiden Substanzen können füglich als Derivate der Isocyansäure aufgefasst werden, welche sich beim ersten Eintreten des Ammoniaks gebildet hätte.



Durch diese Reaktionen werden die Isocyansäure und ihre "Ester" in die Reihen der Phosgenderivate hineingezogen, zu welchem die so nah verwandten Urethane und Harnstoffe schon längst gehörten. Es wird daher eine kurze Uebersicht über die theoretischen Beziehungen, in welchen sich diese Substanzen zu einander und zum Phosgen befinden, an diesem Orte von Nutzen sein.

Betrachtet man, für den Augenblick, das Phosgen als Chlorid der Chlorameisensäure, so wird der Chlorameisen-säureäthylester natürlich dasjenige Substitutionsprodukt sein, in welchem das die Hydroxylgruppe ersetzende Chlor-atom wiederum durch die Aethoxylgruppe verdrängt ist. Das Urethan hingegen ist der *Ester*, der Harnstoff das *Amid*, der Amidoameisensäure oder Carbaminsäure. Michler's Harnstoffchloride sind hier als die Chloride der zweifach alkylirten Carbaminsäuren aufzuführen. Doch giebt es nicht nur dialkylirte Carbaminsäurechloride: wie Leuckart<sup>2</sup> sehr richtig bemerkt, kann man das sogenannte Chlorid der Cyan-

<sup>1</sup> Siehe Seite 3 [p. 179 of this vol.].

<sup>2</sup> Leuckart, *Berichte*, **18**, 874 (1885).

NH.H  
säure nach der Formel | auffassen, und ist sogar bei  
CO.Cl

dem von ihm beobachteten Salze des Phenylcyanats nur  
NC<sub>6</sub>H<sub>5</sub>.H  
eine Formel denkbar | . Wir hätten in diesen wohl-  
CO.Cl

definirten Körpern die Chloride der typischen und der einfach-substituirten Carbaminsäure. Dieselben sind jedoch nicht sehr beständig, da sie gerne Salzsäure [22] abspalten und das innere Anhydrid, das *Lactam*, der Säuren bilden. Es wären hiermit die Isocyansäure als Lactam der Carbaminsäure, das Carbanil als Lactam der Phenylcarbaminsäure auf zufassen. Harnstoffe und Urethane entstehen daraus durch Anlagerung von Aminen resp. Alkoholen.

Folgende Tabelle möge veranschaulichen, wie die hauptsächlichsten Derivate des Phosgens sich von demselben und von einander ableiten: —

Aus den primären Phosgen-Derivaten	Cl COOC <sub>2</sub> H <sub>5</sub>	NH.H CO.Cl	NC <sub>6</sub> H <sub>5</sub> H CO Cl	N(CH <sub>3</sub> ) <sub>2</sub> CO Cl
entstehen unter Einwirkung von H <sub>2</sub> O	OH COOC <sub>2</sub> H <sub>5</sub>	NH.H    CO OH	NC <sub>6</sub> H <sub>5</sub> H    CO OH	N(CH <sub>3</sub> ) <sub>2</sub> COOH nicht bekannt
von C <sub>2</sub> H <sub>5</sub> OH	OC <sub>2</sub> H <sub>5</sub> COOC <sub>2</sub> H <sub>5</sub>	NH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	NC <sub>6</sub> H <sub>5</sub> H COOC <sub>2</sub> H <sub>5</sub>	N(CH <sub>3</sub> ) <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>
von NH <sub>3</sub>	NH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	NH <sub>2</sub> CO.NH <sub>2</sub>	NC <sub>6</sub> H <sub>5</sub> H CONH <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub> CONH <sub>2</sub>

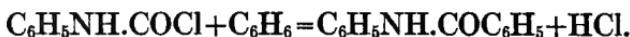
etc.

etc.

Lassen sich nun auch die Wurtz'schen, die Friedel und Crafts'schen Reaktionen des Phenylkerns mit Chlorkohlenoxyd auf die primären Derivate des letzteren ausdehnen?

Für die Chlorameisensäureester ist diese Frage schon längst in ausgiebigster Weise bejaht worden. Leuckart,<sup>1</sup> der zuerst die substituirten Carbaminsäurechloride als solche aussprach, hat uns auch mit einer derartigen Anwendung derselben vertrauter gemacht.

[23] Wenn eine Mischung von Phenylcyanat und Benzol mit Aluminiumchlorid versetzt wird, bildet sich Benzanilid, und ebenso entsteht aus Phenylcyanat mit den Homologen des Benzols immer das Anilid der entsprechenden Säure. Da die Reaktion nur in Gegenwart von Aluminiumchlorid stattfinden will, bemerkt Leuckart, dass die einfachste Erklärung in der Bildung des "salzsauren Carbanils" und der darauffolgenden Einwirkung dieses Säurechlorids nach der Friedel und Crafts'schen Reaktion zu suchen sei:—



Leider fehlen zur Zeit noch Angaben über das Verhalten der Michler'schen disubstituirten Carbaminsäurechloride bei der Aluminiumchlorid-Reaktion; ein obigem analoges Verhalten wäre der beste Beweis für die Richtigkeit der Leuckart'schen Annahme.<sup>2</sup>

#### SPEZIELLE ANWENDUNGEN

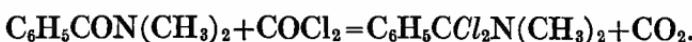
Wenn auch im Vorhergehenden die Aufzählung der für das Gebahren des Phosgens typischen Reaktionen erschöpft ist, sind noch einige spezielle Anwendungen anzuführen, der Resultate wegen, welche dabei erzielt wurden, insbesondere der Bildung von Körpern die zu den Säurederivaten des Harnstoffs gerechnet werden.

Die Säureamide zeigen für das Phosgen nicht die gleiche

<sup>1</sup> Leuckart, *loc. cit.*

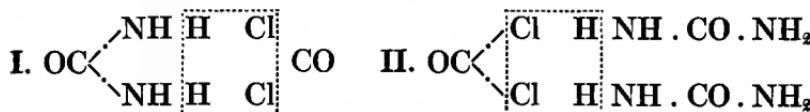
<sup>2</sup> Seitdem ich obiges geschrieben, hat sich auch diese Lücke ausgefüllt. Lellmann und Böhner [Berichte, 19, 3231 (1886)] haben das Diphenylcarbaminsäurechlorid in Gegenwart von Aluminiumchlorid auf Benzol einwirken lassen und Diphenylbenzamid erhalten.

Reaktionsfähigkeit wie die Amine. Wenigstens ist eine höhere Temperatur notwendig und entstehen viele Nebenprodukte. Bei primären Amiden lässt sich allerdings der Wasserstoff der Amidogruppe noch ersetzen: Schmidt<sup>1</sup> hat durch Erhitzen von Acetamid und von Benzamid mit Phosgen Diacetyl- resp. [24] Dibenzoyl-Harnstoff erhalten, obwohl auch hierbei Chlorid und Nitril der Säuren in erheblichen Mengen auftraten. Beim Acetanilid, hingegen scheint die Reaction überhaupt noch nicht gelungen zu sein. Beim Dimethylbenzamid findet der Austausch statt:<sup>2</sup> —

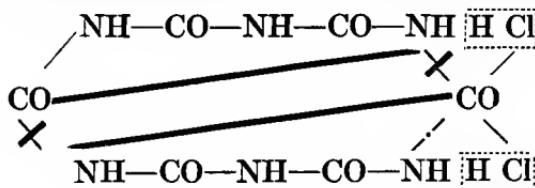


Solche Körper lassen sich aber auf anderen Wegen müheloser herstellen.

Wenn Harnstoff, das Amid der zweibasischen Kohlensäure, mit Phosgen erhitzt wird, kann man zweierlei Reaktionen erwarten:



Nach Schmidt<sup>3</sup> entsteht beim zweitägigen Erhitzen, unter hohem Druck, auf 100°, nur die letztere Verbindung, die er Carbonyldiharnstoff nennt. Ebenso entsteht aus Phosgen und Biuret bei 60° das Carbonyldibiuret. Erhitzt man letzteres nochmals mit Phosgen so erhält man fast reine Cyanursäure, was Schmidt durch folgendes Bild erklärt:



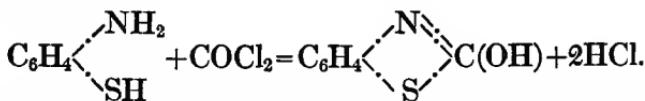
<sup>1</sup> Schmidt, *Journ. prakt. Chem.* [2], 5, 35 (1872).

<sup>2</sup> Hallmann, *Berichte*, 9, 846 (1876).

<sup>3</sup> Schmidt, *Journ. prakt. Chem.* [2], 5, 39 (1872).

Carbonyldiharnstoff liefert mit Phosgen bei 170° nur theilweise Cyanursäure. Es entsteht ein weisses Nebenprodukt, von derselben Zusammensetzung; ob es mit der Cyanursäure isomer oder polymer ist, weiss man noch nicht. Schmidt nennt es Dicyanursäure.

Es ist zu bemerken, dass diese Synthesen der gewöhnlichen Cyanursäure als gute Argumente für die Iso-Konstitution derselben gelten. Die Diskussion dieser Konstitutionsfrage [25] gehört nicht hierher: wohl aber will es mir scheinen dass diesen Synthesen als Beweismittel nicht allzuviel Werth beizulegen ist. Erstens kann man, so lange ein unbekanntes Isomer als Nebenprodukt auftritt, nicht entscheiden, ob es die gewöhnliche Cyanursäure ist, welche auf der glattesten Weise entsteht. Zweitens bedingt die Reaktion, wie oben angegeben, einen Zerfall eines sehr ausgedehnten Moleküls, wobei Umlagerungen keineswegs auszuschliessen sind. Zudem sind Reaktionen des Phosgens nicht unbekannt, in denen eine solche Umlagerung bei gewöhnlicher Temperatur freiwillig eintritt. Ich habe dies selber einmal beim Zusatz von in Benzol gelöstem Phosgen zu o-Amidophenylmerkaptan schön beobachten können. Sofort und *quantitativ* erfolgte die Reaktion —

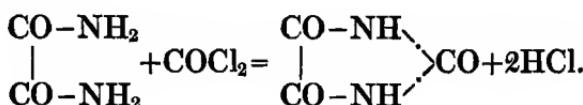


Es war also in der Kälte dieselbe Wanderung eines Wasserstoffatoms vom Stickstoff zum Sauerstoff erfolgt, die man zur Erklärung einer Synthese der normalen Cyanursäure mittels Phosgen annehmen müsste.

Oxamid mit Phosgen erhitzt, gab nach Schmidt nur Carbonyldiharnstoff, unter gleichzeitiger Entwicklung von viel Kohlenoxid —



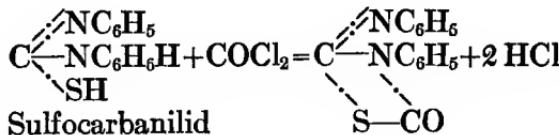
Basarow<sup>1</sup> hingegen will auf diese Art Parabansäure erhalten haben —



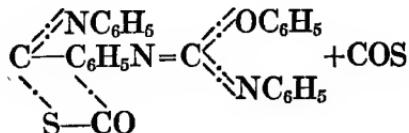
Während Phosgen auf Harnstoff erst bei beträchtlicher Wärme einwirkt, geschieht dies nach Will<sup>2</sup> bei den Thioharnstoffen sofort, obwohl mit anderen Resultaten. Es deuten [26] dieselben sogar auf eine abweichende Konstitution der geschwefelten Harnstoffe von den sauerstoffhaltigen. Verschiedene Umstände überzeugten Will, dass die Reaktion beim Sulfocarbanilid den Verlauf —



nicht haben kann, sondern, dass das Endprodukt derart ist, dass man als einfache Erklärung folgende Gleichung annehmen möchte —



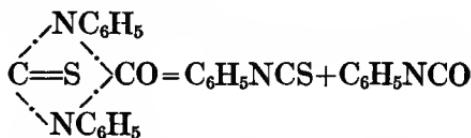
Als vornehmster Grund diente das Verhalten der Substanz beim Erhitzen



<sup>1</sup> Basarow, *Berichte*, 5, 477 (1872).

<sup>2</sup> W. Will, *Berichte*, 14, 1486 (1881).

Wäre die Formel symmetrisch, so müssten als Spaltungsprodukte erwartet werden



Man wird sich erinnern, dass auch andere Forscher zur Annahme derselben Formel für die Thioharnstoffe geleitet worden sind, wie Will.<sup>1</sup> Die Untersuchungen des Letzteren erstreckten sich nur auf die substituirten Körper dieser Gruppe. Indem ich versuchte, zur Vervollständigung auch das einfache [27] Thiocarbamid zu ähnlicher Reaction zu bringen, fand ich, dass es selbst bei den höchsten Temperaturen die es erträgt, vom Phosgen nicht beeinflusst wird.

Es existiren noch eine Anzahl amidähnliche Substanzen, in denen der Sauerstoff des Säureradikals durch eine Imidgruppe ersetzt ist, die Amidine und Guanidine. Von diesen war bisher nur das Triphenylguanidin auf sein Verhalten mit Chlorkohlenoxyd geprüft worden.<sup>2</sup> Auf Veranlassung des Herrn Professors A. W. Hofmann habe ich mich bemüht, auch aus Amidinen Phosgenderivate darzustellen, und werde ich im "Experimentellen Theil" über diese und andere davon herührende Versuche weitläufiger reden. Meinen Bericht über die Phosgenderivate würde ich jedoch, bei der grossen Anzahl derselben die im vorausgehenden keine Ermahnung finden konnten, nicht für vollständig erachten, ohne ein Verzeichniss der mir bekannten einschlägigen Litteratur.

<sup>1</sup> So Liebermann, *Berichte*, **12**, 1588 (1879).

<sup>2</sup> Michler und Keller, *Berichte*, **14**, 2181 (1881).

## [28] LITTERATUR-VERZEICHNISS

## DARSTELLUNG DES PHOSGENS

Aus Kohlenoxyd und Chlor. Davy, *Phil. Trans. Royal Society*, 1812, 144.

Willm und Wischin, *Zeitschr. f. Chem.* 1868, 5.

Paternò, *Gazz. Chim. Ital.* 8, 233 (1878).

Goebel, *Berzelius Jahresbericht*, 16, 162.

Hofmann, *Annalen*, 70, 139 (1849).

Aus Schwefelkohlenstoff und Unterchlorigsäureanhydrid. Schützenberger, *Berichte*, 2, 219 (1869).

Aus Schwefelkohlenstoff, Chlor und Schwefelsäure.

Berzelius, *Lehrbuch der Chemie*, Bd. 2.

Kolbe, *Annalen*, 54, 148 (1845).

Aus Tetrachlorkohlenstoff. Schützenberger, *Comptes Rendus*, 66, 747; (1868). 69, 352 (1869).

Armstrong, *Berichte*, 3, 730 (1870).

Gustavson, *Zeitschr. f. Chem.*, 1871, 615.

Aus Chloroform. Dewar und Cranston, *Chem. News*, 20, 174 (1869).

Emmerling und Lengyel, *Berichte*, 2, 547 (1869).

Aus Perchlorameisensäuremethylester. Cahours, *Ann. chim. et phys.* [3], 19, 352 (1847).

Aus Trichloressigsäurem Natrium.

Kolbe, *Annalen*, 54, 150 (1845).

Henry, *Berichte*, 12, 1845 (1879).

## EIGENSCHAFTEN

Berthelot, *Compt. Rend.* 87, 571 (1878).

Thomsen, *Berichte*, 16, 2619 (1883).

Berthelot, *Annalen*, 156, 228 (1870).

## [29] REAKTIONEN MIT KOHLENWASSERSTOFFEN

## Darstellung von Säurechloriden und Ketonen

Mit Kohlenwasserstoffen der Fettreihen.

Harnitz-Harnitzky, *Compt. Rend.* 60, 923 (1865).

Berthelot, *Bull. Soc. Chim. n. s.* 13, 9 (1870).

De Clermont et Fontaine, *ibid. seq.*

Mit Zinkmethyl. Butlerow, *Berichte*, 3, 426 (1870). Siehe auch Butlerow, *Organische Chemie*, S. 297.

Mit Benzol. Harnitz-Harnitzky, *Compt. Rend.* 58, 748 (1864).

Berthelot, *Bull. Soc. Chim. n. s.* 13, 9 (1870).

Friedel, Crafts und Ador, *Berichte*, 10, 1854 (1877).

Mit Toluol. Ador und Crafts, *Berichte*, 10, 2173 (1877).

Xylol. Ador und Rilliet, *Berichte*, 11, 399 (1878).

Elbs und Olberg, *Berichte*, 19, 408 (1886).

- Mit Anthracen. Graebe und Liebermann, *Berichte*, **2**, 678 (1869).  
 Behla. *Berichte*, **18**, 3169 (1885).
- Mit Phenanthren. *Ibid.*  
 Brombenzol. Wurtz, *C. R.* **68**, 1298 (1869).  
 Thiophen. Gattermann, *Berichte*, **18**, 3013 (1885).  
 Pyrrol. Ciamician und Magnaghi, *Berichte*, **18**, 414 (1885). .

### REAKTIONEN MIT ALKOHOLEN UND PHENOLEN

#### Darstellung von Chlorameisensäure- und Kohlensäure-Estern

- Mit Methylalkohol. Dumas und Peligot, *Ann. chim. et phys.* **58**, 52 (1835).  
 Hentschel, *Berichte*, **18**, 1177 (1885).
- Mit Aethylalkohol. Dumas, *Ann. chim. et phys.* **54**, 226 (1833).  
 Propylalkohol. Roemer, *Berichte*, **6**, 1101 (1873).  
 Isopropylalkohol. E. Mylius, *Berichte*, **5**, 972 (1872).  
 Isoamylalkohol. Medlock, *Quart. Journ. Chem. Society*, **1**, 368 (1849).  
 Glycol. Nemirovsky, *Journ. prakt. Chem.* **28**, 439 (1843).  
 Glycolchlorhydrin. Nemirovsky, *Journ. prakt. Chem.* **31**, 173 (1844).  
 Glycolsäureester. Heintz, *Annalen*, **154**, 257 (1870).  
 Milchsäure. Kempf, *Journ. prakt. Chem.* [2], **1**, 412 ff. (1870).  
 Epichlorhydrin. Kempf, *ibid.*  
 Phenol. Kempf, *Patent des Deutschen Reiches*, 30172. *Berichte*, **18**, Ref. 40. 17 (1885).
- Mit Kresol. Kempf.  
 Thymol. Kempf.  
 Nitrophenol. Kempf.
- [30] Mit Eugenol. Salicylaldehyd. Löwenberg, *Inaug.-Diss.* Berlin, 1885.  
 Resorcin. Birnbaum und Lurie, *Berichte*, **14**, 1754 (1881).  
 Merkaptanen. Salomon, *Journ. prakt. Chem.* [2], **6**, 433 ff. (1872).  
**7**, 254 (1873).  
 Schöne, *Journ. prakt. Chem.* [2], **30**, 416 (1884).
- Mit Thiophenol. Löwenberg.  
 Naphtol,  $\alpha$ ,  $\beta$ . Löwenberg.

### REAKTIONEN MIT ALDEHYDEN UND SÄUREN

#### Chlorirung derselben

- Mit Acetaldehyd. Harnitz-Harnitzky, *Annalen*, **111**, 192 (1859).  
 Friedel, *Compt. Rend.* **60**, 930 (1865) und *Ann. chim. et phys.* [4], **16**, 403 (1869).  
 Kraut, *Annalen*, **147**, 107 (1868).  
 Stacewitz, *Zeitschr. f. Chem.* 1869, 321.  
 Kekulé und Zincke, *Annalen* **162**, 125 (1872).  
 Eckenroth, *Berichte*, **18**, 518 (1885).

Mit Benzaldehyd. Kempf.

Aceton. Wroblewski, *Zeitschr. f. Chem.* [2], 4, 565.

Essigsäure. Kempf.

V. Meyer, *Annalen*, 156, 271 (1871).

### REAKTIONEN MIT PRIMÄREN AMINEN

#### *Darstellung symmetrischer Harnstoffe*

Mit Ammoniak. J. Davy, *Phil. Trans.* 1812, 144.

Régnault, *Ann. chim. et phys.* 69, 180 (1809).

Natanson, *Annalen*, 98, 287 (1856).

Bouchardat, *Compt. Rend.* 69, 94 (1869).

Fenton, *Journ. Chem. Soc.* 35, 793 (1879).

Mit Anilin. Hofmann, *Berichte*, 57, 267 (1846).

Orthotoluidin. Girard, *Berichte*, 6, 444 (1873).

Amidopropylbenzol. Francksen, *Berichte*, 17, 1224 (1884).

Amidoisobutylbenzol. Pahl, *Berichte*, 17, 1240 (1884).

Benzidin. Michler und Zimmermann, *Berichte*, 14, 2174 ff. (1881).

m-Phenylendiamin. Michler und Zimmermann.

p-Amidodimethylanilin. Michler und Zimmermann.

Anisidin. Mühlhäuser, *Berichte*, 13, 922 (1880).

Amidoazobenzol. Berju, *Berichte*, 17, 1400 (1884).

### [31] REAKTIONEN MIT SEKUNDÄREN AMINEN

#### *Darstellung von Carbaminsäurechloriden und Harnstoffen*

Mit Dimethylanin. Michler und Escherich, *Berichte*, 12, 1162 (1879).

Diäthylamin. Michler, *Berichte*, 8, 1665 (1875).

Methylaminlin. Michler und Zimmermann, *Berichte*, 12, 1165 (1879).

Aethylendiphenyldiamin. Michler und Keller, *Berichte*, 14, 2181 (1881).

Diazoamidbenzol } Sarauw, *Berichte*, 14, 2443 (1881).

Diazobenzolparatoluid }

Diphenylamin. Michler, *Berichte*, 9, 396 (1876).

Willm und Girard, *Berichte*, 9, 449 (1876).

### REAKTIONEN MIT TERCIÄREN AMINEN

#### *Bildung amidirter Säurechloride und Benzophenone*

Mit Dimethylanilin. Michler, *Berichte*, 9, 4500, 716 (1876).

Michler und Dupertius, *Berichte*, 9, 1899 (1876).

Patente, *Berichte*, 17 (1884). Ref. 40, 339, 60. 18 (1885). Ref. 7.

Hofmann, *Berichte*, 18, 770 (1885).

Mit Diäthylanilin. Michler, *Berichte*, 8, 1665 (1875).

Michler und Gradmann, *Berichte*, 9, 1912 (1876).

## REAKTIONEN MIT AMMONIUMSALZEN

*Bildung von Isocyanaten*

- Mit salzs. Anilin. Hentschel, *Berichte*, **18**, 1178 (1885).  
 Methylamin. Gattermann und Schmidt, *Berichte*, **20**, 118 (1887).  
 Aethylamin. Dieselben.  
 m-Phenylendiamin. Gattermann und Wrampelmeyer, *Berichte*, **18**, 2604 (1885).  
 Mit Benzidin. Snape, *Journ. Chem. Soc.* **49**, 255 (1886).  
 m-Toluylendiamin. Snape.  
 Phenylhydrazin. Snape.

## REAKTIONEN MIT AMIDEN

*Bildung von Ureiden*

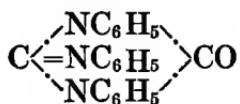
- Mit Acetamid. Schmidt, *Journ. prakt. Chem.* [2], **5**, 89 ff. (1872).  
 Oxamid. Schmidt.  
 Basarow, *Berichte*, **5**, 477 (1872).  
 Mit Benzamid. Schmidt.  
 [32]  
 Mit Dimethylbenzamid. Hallmann, *Berichte*, **9**, 846 (1876).  
 Harnstoff. Schmidt.  
 Biuret. Schmidt.  
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## REAKTIONEN MIT ANDEREN KÖRPERN

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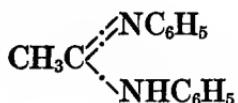
## [33] EXPERIMENTELLER THEIL

DIE Versuche von Michler und Keller<sup>1</sup> über die Einwirkung des Phosgens auf das symmetrische Triphenylguanidin haben zu keinem erheblichen Resultate geführt, da die entstehenden Substanzen die Kriterien der Reinheit nicht besassen. Man muss sogar bezweifeln, dass der von ihnen erhaltenen bei 134° schmelzenden Substanz wirklich die Formel



zukomme, da dieselbe von Stojentin<sup>2</sup> für seinen wohldefinierten, bei 190° schmelzenden Körper in Anspruch genommen wird, welchen er aus dem Guanidin mittels des Aethoxalylchlorids erhalten hat.

Der Versuch sollte nun zeigen, ob ein Amidin, vermöge seiner einfacheren Bauart, sich der Reaktion williger hingeben wollte. Naturgemäß fiel meine Aufmerksamkeit zuerst dem Aethenyldiphenyldiamin



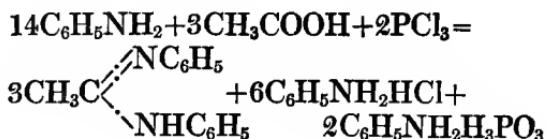
zu, welches durch die Eigenschaften der leichten Darstellung und ziemlichen Beständigkeit vor den meisten Körpern dieser Klasse hervorstach.

Im Laufe dieser Arbeit habe ich die verschiedenen Darstellungsweisen, die man für das Aethenyldiphenyldiamin vorgeschlagen hat, prüfen können, und bin zu der Ueberzeu-

<sup>1</sup> Berichte, 14, 2181 (1881).

<sup>2</sup> Journ. prakt. Chem. 32, 29 (1844).

gung [34] gelangt, dass diejenige, welche A. W. Hofmann<sup>1</sup> bei der ersten Beschreibung dieser Substanz empfohlen hat, am raschesten und sichersten zum Ziele führt, wenn auch die Reaktion einen ziemlichen Aufwand an Ausgangsmaterial erfordert



Ich verfuhr gewöhnlich so, dass ich 35 Gramm Anilin und 13 Gramm Eisessig in einem Kolben vermischt und zu der erkalteten Lösung nach und nach 25 Gramm Phosphortrichlorid gab. Die Anfangs heftige Reaktion wurde durch Abkühlen gedämpft. Alsdann wurde der Kolben, mit einem Rückflussküller versehen, in einem Oelbade erwärmt, dessen Temperatur langsam auf 165° erhöht wurde. Hier verblieb derselbe, bis das Aufhören der Salzsäureentwicklung das Ende der Reaktion anzeigen sollte. Die Schmelze löste sich fast vollkommen in kochendem Wasser; beim Erkalten krystallisierten oft geringe Mengen Acetanilid aus. Das aus der filtrirten Lösung mittelst Ammoniak gefällte Amidin brauchte zur Reinigung nur noch einmal aus Alkohol umkrystallisiert zu werden. Die Ausbeute betrug die Hälfte des Gewichts des angewandten Anilins und war folglich nach obiger Gleichung fast theoretisch.

#### EINWIRKUNG DES PHOSGENS IM UEBERSCHUSS AUF AETHENYLDIPHENYLDIAMIN

Zehn Gramm der wohlgetrockneten und feingepulverten Base wurden mit einem Ueberschuss verflüssigten oder auch in Benzol gelösten Phosgens in einem Glasrohre eingeschlossen und 4–5 Stunden lang im Wasserbade erwärmt; die Tempera-

<sup>1</sup> A. W. Hofmann, *Monatsberichte der Berliner Akad.* 1865, 249.

tur durfte  $60^\circ$  nicht übersteigen. Der Röhreninhalt hatte hierauf eine tiefgelbe Farbe angenommen und bestand zu zwei Dritteln aus salzsaurem Amidin; mit warmem Benzol oder Aether liess [35] sich eine Substanz ausziehen, welche beim Verdunsten des Lösungsmittels gewöhnlich als ein klebrignes, gelbes Harz zurück blieb. Auf Zusatz einiger Tropfen kalten, absoluten Alkohols verwandelte sie sich jedoch in einen Krystallbrei, aus welchem das Oel durch Abpressen entfernt wurde. Nunmehr wurden die Krystalle, unter sorgfältiger Vermeidung des Siedens, aus verdünntem Alkohol umkristallisiert, bis sie den gelben Stich verloren und bei  $110^\circ$  konstant schmolzen. Die Substanz bildete alsdann kleine farblose Nadeln und erwies sich als chlorhaltig. Zur Analyse wurde sie noch mit Aether gewaschen und bei  $110^\circ$  getrocknet.

- I. 0.3013 Gramm Substanz gaben 0.6335 Gramm  $\text{CO}_2$  und 0.0979 Gramm  $\text{H}_2\text{O}$ ;
- II. 0.2746 Gramm Substanz gaben 20.75 ccm N,  $t = 24.25^\circ$ ,  $B_0 = 755$  mm,  $7 = 16.6$  mm;
- III. 0.3107 Gramm Substanz gaben 0.2705 Gramm  $\text{AgCl}$  nach Carius.<sup>1</sup>

Diese Analysen wiesen unzweideutig auf eine Formel



	Verlangt für:		Gefunden:		
	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{Cl}_2\text{O}_2$		I	II	III
C	192	57.31	57.34		
H	12	3.58	3.61		
N	28	8.36		8.46	
Cl	71	21.19			21.54
O	32	9.56			
	<hr/>	<hr/>			
	335	10.000			

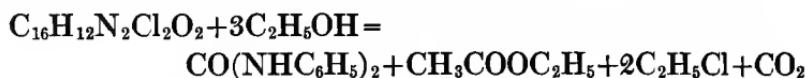
<sup>1</sup> Die Chlorsilber-Niederschläge wurden auf einem tarirten Gooch'schen Platintrichter gesammelt, bei  $120^\circ$  getrocknet, und gewogen.

Es hatte also folgende Reaktion stattgefunden: —



Aus 10 Gramm Amidin liessen sich 3 Gramm des neuen Körpers, also 60 Prozent der theoretischen Menge gewinnen. Der gute Ausfall des Verfahrens hängt aber wesentlich davon ab, dass der Körper in Lösungsmitteln keiner hohen Temperatur [36] ausgesetzt werde, da seine Beständigkeit nur sehr gering ist. Seine Zersetzbarkheit trat auch störend zu Tage, als ich seine Konstitution durch Darstellung von Derivaten erforschen wollte.

Von kochendem Wasser wird er nicht angegriffen, von Säuren und Alkalien hingegen in das Amidin zurückverwandelt. Beim Kochen mit Alkohol treten sofort Essigester und Chloräthyl auf; beim Erkalten scheiden sich kleine Nadeln in Menge aus, welche chlorfrei sind, bei  $234^\circ$  schmelzen und sich hierdurch, sowie durch den beim Erhitzen auftretenden Carbanilgeruch, als Carbanilid charakterisiren. Die Zersetzung hat hier den Amidinrest selber ergriffen: —



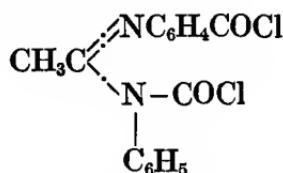
Es wurden Versuche gemacht, die Chloratome durch Aminogruppen zu ersetzen. Da sich weder wässriges noch alkoholisches Ammoniak bewährten, wurde der Körper in Benzol gelöst und trockenes Ammoniakgas hindurchgeleitet. Es schied sich unter Erwärmung eine der Chlormenge genau entsprechende Quantität reinen Salmiaks aus. Die Lösung enthielt aber bloss Aethenyldiphenyldiamin, was sich nur durch die folgende Gleichung erklären lässt: —



Analog entstehen mit heissem Anilin das Amidin, salzaures Anilin und Carbanilid.

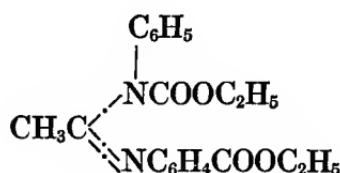
Für sich über ihren Schmelzpunkt erhitzt, zersetzt sich die Substanz bei 150° unter reichlicher Entwicklung von Phosgengas und von Phenylisocyanat.

Diese Thatsache ist eine wesentliche Stütze zur Annahme einer Konstitution welche sonst noch durch das von Michler entdeckte Verhalten der sekundären und tertiären Aniline gegen Phosgen geboten erscheint



[37] Erfreulicherweise habe ich diese Annahme auch ferner bestätigen können, durch Darstellung eines

*Esters.* Es muss hierbei natürlich jede Erwärmung vermieden werden. Eine 2 Atomen entsprechende Menge Natrium wurde in Aethylalkohol gelöst und nach dem Erkalten die alkoholische Lösung des Chlorids [1 Molekül] allmählig unter Abkühlung hinzugesetzt. Von dem sich sofort abscheidendem Kochsalz abfiltrirt und über Schwefelsäure im luftleeren Raume verdunstet, hinterliess die Flüssigkeit eine chlorfreie Substanz, welche nach zweimaligem Umkristalliren aus Aether harte, glänzende, rhombische Krystalle bildet, die bei 90.5° schmelzen. Der Analyse der *in vacuo* getrockneten Substanz zufolge, ist in der That der Ester entstanden.



I. 0.2965 gr Substanz gaben 0.7363 gr CO<sub>2</sub> und 0.1730 gr H<sub>2</sub>O.

II. 0.1775 gr Substanz gaben 12.7 ccm N.  $t=10^{\circ}$

$B_0 = 755.8$  mm,  $\tau = 7.1$  mm.

III. 0.2020 gr Substanz gaben 14.4 ccm N.  $t=12.5^{\circ}$

$B_0 = 772.8$  mm,  $\tau = 8.4$  mm.

	Verlangt für:		Gefunden:		
	$C_{20}H_{22}N_2O_4$		I	II	III
C	240	67.79		67.74	
H	22	6.21		6.48	
N	28	7.91			8.51      8.60
O	64	18.08			
	<hr/>	<hr/>			
	354	99.99			

Selbst in der Kälte ist der Ester in alkoholischer Lösung unbeständig. Von wässrigem Ammoniak wird er, ebenso wie das Chlorid, in das Amidin zurückverwandelt. Da ich nun auf diesem Wege keine Amidoverbindungen zu [38] gewinnen vermochte, bemühte ich mich eine directe Anlagerung von Cyansäure resp. Rhodanwasserstoffsäure an das Amidin, welche zu dem gesuchten ähnlichen Körpern geführt hätte, zu bewerkstelligen. Auch diese Versuche schlugen fehl, da das Cyanat des Amidins schon in kalter, wässriger Lösung Kohlensäure und Ammoniak abspaltet; das Rhodanat, welches ein Harz darstellt, ist zwar beständiger, lagert sich jedoch nicht in den Thioharnstoff um, sondern verwandelt sich oberhalb  $100^{\circ}$  in ein tibelriechendes Oel.

Uebrigens lässt sich auch der Ester nicht direct aus dem Amidin, durch die sie sonst so bequeme Anwendung des Chlorameisensäureesters, gewinnen. Eine Einwirkung desselben findet erst bei  $60^{\circ}$  statt; nach Verdunsten der vom salzsäuren Amidin befreiten Flüssigkeit verbleibt eine halbfeste Masse, welche an Aether kleine Mengen eines nicht krystallisirenden Oels abgiebt und im Uebrigen aus Carb-anilid besteht.

EINWIRKUNG VON PHOSGEN AUF ÜBERSCHÜSSIGES  
AETHENYLDIPHENYLDIAMIN

*Aethenylimidobenzanilid*

Wenn man, statt auf oben angegebener Weise zu verfahren, Phosgenas in eine siedende Chloroformlösung des Amidins einleitet, so ändert sich auch das Resultat. Es entsteht eine chlorfreie Verbindung, welche ihre Existenz dem Zusammentreten von einem Molekül Phosgen und einem Molekül Amidin verdankt.



Dieselbe entsteht daher auch, und zwar in glatterer Reaktion, wenn Phosgen in Benzol gelöst bei 80° auf einen Ueberschuss von Aethenyldiphenyldiamin einwirkt. Nach einstündiger Erhitzung wird das Einschlusrohr geöffnet, die Flüssigkeit vom salzsäuren Amidin befreit und das Benzol verdunstet. Der krystallinische Rückstand wird mit kalter, starkverdünnter Salzsäure von unveränderter Base befreit und [39] umkristallisiert. Er ist in Aether, Alkohol, Chloroform und Benzol löslich und krystallisiert besonders aus letztgenanntem Lösungsmittel in grossen, glänzenden Tafeln vom Schmelzpunkt 118°. Er ist viel beständiger als das chlorhaltige Derivat.

Die Analyse der bei 100° getrockneten Substanz ergab Zahlen aus welchen die Formel C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O berechnet wurde.

- I. 0.1874 gr Substanz gaben 0.5314 gr CO<sub>2</sub> und  
0.0948 gr H<sub>2</sub>O.
- II. 0.2031 gr Substanz gaben 0.5706 gr CO<sub>2</sub> und  
0.1024 gr H<sub>2</sub>O.
- III. 0.1720 gr Substanz gaben 17.9 ccm N, t=23.3°,  
 $B_0=758$  mm,  $\tau=16.7$  mm.

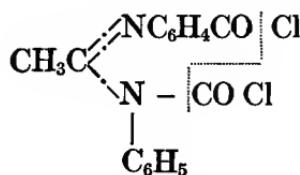
IV. 0.2263 gr Substanz gaben 24 ccm N,  $t=21^\circ$ ,  $B_0=757$  mm,  
 $\tau=14.5$  mm.

	Verlangt für:		Gefunden:			
	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O		I	II	III	IV
C	180	76.27	77.33	76.61		
H	12	5.08	5.62	5.60		
N	28	11.85			11.73	12.07
O	16	6.80				
	236	100.00				

Es lässt diese Zusammensetzung nur eine Auffassung zu



Dieser Körper, den ich *Aethenylimidobenzanilid* benennen will, dürfte auch bei der schon erwähnten Phosgenabspaltung entstehen, welche das Chlorid beim Erhitzen erleidet



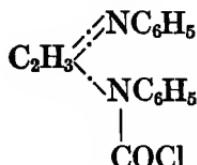
Die stets zugleich auftretende Carbanilentwicklung verhindert jedoch seine Isolirung. Wird das reine Aethenylimidobenzanilid [40] über seinen Schmelzpunkt erhitzt, so bräunt es sich bald, und entwickelt etwas Isonitril. Mit verdünnter Salzsäure gekocht spaltet es sich vollkommen, wobei Anilin und Phenylcyanat als Produkte auftreten.



Diese Reaktionen des Phosgens sind die ersten die mit einer Substanz ausgeführt worden sind, welche je einen sekundären und einen tertiären Anilinrest enthält. Sie zeigen die

Gleichwerthigkeit der beiden Michler'schen Reaktionen an, insofern als bei einer niedrigen Temperatur der Eintritt der Carbonylgruppe in den Phenylkern ebenso rasch erfolgt wie in den Imidorest.

Andernfalls müsste auch ein Körper —



aufgetreten sein, der sich jedoch nicht beobachten liess.

Ich wollte nunmehr diese Reaktion auch auf andere Amidine von analoger Constitution ausdehnen, und stellte zu diesem Zwecke das Benzenyldiphenyldiamin dar. Wiederum bewährte sich Hofmann's Darstellungsweise am besten, mit der Modification, das man fertiges Benzalid und Anilin der Einwirkung des Phosphortrichlorids aussetzt; die Schmelze konnte nur mit kochender concentrirter Salzsäure ausgezogen werden. Die Einwirkung des Chlorkohlenoxyds auf dieses Amidin liess sich aber nicht verfolgen, da die Reaktionsprodukte allzu geringe Krystallisationsfähigkeit zeigten.

Das Methenyldiphenyldiamin, welches ebenfalls von Hofmann dargestellt worden ist, ist wenig beständig. Es erschien daher angemessen, das Propionamidin, behufs Prüfung dieser Reaktion, darzustellen: da dieser Körper noch nicht bekannt ist, habe ich ihn und, zur Vervollständigung der Reihe, auch die homologen Butenyl- und Isobutenyl-Amidine analysiert und ihre Eigenschaften beobachtet.

#### [41] PROPYNYLDIPHENYLDIAMIN

Zur Darstellung wird genau wie beim Aethenylderivat verfahren und zwar werden wiederum 3 Theile Anilin, 1

Theil Propionsäure und 3 Theile Phosphortrichlorid angewandt. Die salzaure Lösung lässt auf Alkalizusatz die Base als helles Oel fallen, welches nur langsam fest wird. Dieselbe ist in Alkohol und Aether noch löslicher als das Aethenylamidin, und krystallisiert in langen weissen Nadeln, die bei 105° schmelzen.

Behufs Gewinnung des Platindoppelsalzes wurde die Base in starkverdünnter Salzsäure aufgelöst und mit Platinchloridlösung versetzt. Der alsbald erfolgende gelbe Niederschlag ist in Wasser und Weingeist wenig, in absolutem Alkohol gar nicht, in starker Salzsäure dagegen sehr leicht löslich.

Er wurde aus salzsäurehaltigem Alkohol umkrystallisiert, mit absolutem Alkohol gewaschen und bei 100° getrocknet. Das Salz wurde so in prachtvollen, scharlachrothen Prismen von einiger Grösse erhalten.

0.6119 Gramm Substanz, im Tiegel verbrannt, hinterliessen 0.1395 Gramm Asche.

Verlangt für:	Gefunden:
$(C_{15}H_{16}N_2)_2 \cdot 2HClPtCl_4$	
Pt 22.64	22.79 Procent

#### BUTENYLDIPHENYLDIAMIN

Dasselbe entstand aus 1 Theil Buttersäure, 5 Theilen Anilin und 3 Theilen  $PCl_3$ . Die Ausbeute war, auf die Säure berechnet, theoretisch. Schmelzpunkt der in Nadeln krystallisirenden Base 106.5°.

Das Platindoppelsalz fällt auf Zusatz von Platinchlorid zur salzsäuren Lösung nach einiger Zeit nieder, und hat alsdann eine schwachgelbe Farbe. Es ist in Alkohol und heissem Wasser leicht löslich. Aus ersterem krystallisiert es in gelbrothen, aus letzterem in braunrothen Nadeln, welche [42] bei durchscheinendem Lichte fast farblos erscheinen. Es wurde bei 100° getrocknet und analysirt.

0.5869 Gramm Substanz, im Tiegel verbrannt, hinterliessen 0.1298 Gramm Asche.

Verlangt für:  
 $C_{32}H_{38}N_4PtCl_6$

Pt 21.92

Gefunden:

22.12 Procent

#### ISOBUTENYLDIPHENYLDIAMIN

Die auf ebendieselbe Weise dargestellte Base fällt als Oel aus, welches nur nach längerem Kochen mit Wasser fest wird. Sie ist in heissem und kaltem Wasser unlöslich und lässt sich mit Dampf destilliren. Die Krystalle schmelzen bei 79°. Von kalter konzentrirter oder heißer verdünnter Salzsäure wird dieses Amidin leicht zersetzt, unter Bildung des Isobutenylanilids.

*Platindoppelsalz.* Dasselbe wird aus einer mässig verdünnten Lösung als gelbes Krystallpulver erhalten. Es ist in heissem und kaltem Wasser und in heissem Alkohol löslich.

0.5052 gr bei 100° getrockneter Substanz hinterliessen 0.1109 gr Pt.

Verlangt für:  
 $C_{32}H_{38}N_4PtCl_6$

Pt 21.92

Gefunden:

21.95 Procent

Die Einwirkung des Phosgens auf das Propenyldiphenyldiamin habe ich zwar versucht und einen krystallisirbaren Körper erhalten. Derselbe ist jedoch nur in kleinen Quantitäten erhältlich und sehr zersetzblich. Er wurde aus Aether umkrystallisiert, war jedoch nicht frei von Chlor zu erhalten, obwohl eine Chlorbestimmung zeigte dass dasselbe nur Verunreinigung sei. Eine bei 76° schmelzende Portion wurde analysirt, ohne jedoch Zahlen zu geben aus welchen sich etwas deuten liesse.

Indem nun die Einwirkung des Phosgens auf Amidine,

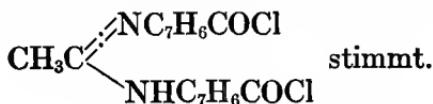
welche sich von Aethenyldiphenylamidin durch die zu ihrer [43] Bildung angewandten Säuren unterscheiden, keine greifbare Resultate geliefert hatte, war es möglich dass sich ein besserer Erfolg bei einem Aethenylamidin erzielen liesse, in welchem an Stelle des Anilins eine homologe Base getreten ist. Ich beschloss daher, Versuche mit Derivaten des Para-resp. Orthotoluidins anzustellen.

#### EINWIRKUNG DES PHOSGENS AUF AETHENYLDI-P-TOLUYL-DIAMIN

Dieses Amidin ist zuerst von Hofmann dargestellt, jedoch von Bernthsen<sup>1</sup> genauer beschrieben worden. Ich befolgte die Vorschrift des Ersteren, und erhielt so leicht ein Produkt dessen Schmelzpunkt 188° mit Bernthsen's Angabe im Einklang stand. Je 10 g des trocknen Amidins wurden mit 2.8 g Carbonylchlorid in Benzollösung 3–4 Stunden lang im Einschlussrohr auf 60° erhitzt. Es hatten sich salzaures Amidin und eine im Benzol lösliche Substanz gebildet, welche nach freiwilligen Verdampfen des Lösungsmittels als gelbes Oel zurückblieb. Zum krystallisiren war dieselbe nur dadurch zu bringen, dass man sie mit einigen Tropfen eiskaltes absoluten Alkohols übergoss, worauf sie zu einem Krystallbrei erstarrte. Sofort zwischen Filtrirpapier abgepresst und mit warmem absoluten Aether behandelt, erwiesen sich jedoch die Krystalle zum grossen Theil als in Aether unlösliches, bei 254° schmelzendes Carbotoluid, während ein kleiner Theil in Lösung ging. Durch Vereinigung der Produkte mehrerer Operationen, und sorgfältiges Umkrystallisiren aus Aether, gelang es mir, eine kleine Menge einer konstant bei 108° schmelzenden Substanz zu isoliren, welche chlorhaltig war und in gut ausgebildeten kurzen Prismen krystallisirte. Die Ausbeute war jedoch so schlecht, dass es

<sup>1</sup> Hofmann, *Annalen*, 184, 364 (1877).

mir nur möglich war, eine einzige Chlorbestimmung auszuführen, deren Resultat allerdings gut auf einen Körper —



[44] 0.2756 gr Substanz gaben nach der Carius'schen Methode 0.2241 gr AgCl.

Verlangt für:  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{Cl}_2\text{O}_2$

Gefunden:

Cl 19.56

20.11 Procent

Die Absicht, auch mit dem Orthoditoluylamidin Versuche anzustellen, musste ich aufgeben, da ich nicht erwarten durfte eine krystallisbare Substanz aus diesem Ausgangsprodukte zu erhalten, welches selber einen sehr niedrigen Schmelzpunkt besitzt. Da dieses Amidin jedoch bisher noch nicht beschrieben worden ist, gebe ich an dieser Stelle meine Beobachtungen wieder.

#### AETHENYLDI-O-TOLUYLDIAMIN

Zur Darstellung verwandelte ich 40 gr Orthotoluidin, 12 gr Eisessig und 25 gr Phosphortrichlorid. Nachdem die Schmelze mit kochendem Wasser ausgezogen war, fiel aus der Lösung, auf Alkalizusatz, ein nichtkrystallisirendes, farbloses Oel aus. Wasserdampf trieb unverändertes Toluidin aus demselben aus; der Rückstand erstarrte jedoch erst nach einigen Tagen, und zwar ohne Spuren einer krystallinischen Struktur. Aus Alkohol und sonstigen Lösungsmitteln schied sich immer ein Oel aus, das alsdann amorph erstarrte. Auch salpetersaure, schwefelsaure, essigsäure und oxalsäure Salze liessen sich auf keine Weise krystallinisch erhalten. Dagegen entstanden schöne Nadeln des salzsäuren Salzes beim Einleiten von Chlorwasserstoffgas in eine trockene ätherische Lösung der Base.

Zur Charakterisirung der Substanz stellte ich das Platin-doppelsalz dar. Es ist dasselbe ein gelbes, in Wasser schwer-lösliches, Krystallpulver, welches sich beim Erhitzen mit Wasser oder Alkohol leicht zersetzt. Ueber Schwefelsäure und dann bei 100° getrocknet und im Porzellantiegel ver-brannt, lieferte es die der Theorie entsprechende Menge Platin. 0.5818 gr Substanz hinterliessen 0.1273 gr Asche.

Verlangt für:  $C_{32}H_{38}N_4PtCl_6$

Gefunden:

Pt 21.92

21.88 Procent

[45] Den Schmelzpunkt der Base fand ich bei 45–47°.

Ehe ich das Feld der Amidine verliess, lag der Wunsch nahe, den Versuch anzustellen, ob nicht noch eine andere Reaktion, die der Cyananlagerung, sich bei denselben anwen-den liesse. Hofmann hatte dieselbe zuerst beim Anilin beob-achtet und dann auch auf Guanidine ausgedehnt.<sup>1</sup> In der That ist sie auch auf das Aethenylidiphenyldiamin anwendbar.

#### EINWIRKUNG DES CYANS AUF DAS AETHENYLAMIDIN

Eine gesättigte ätherische Lösung des Amidins, mit 2–3 Tropfen Wassers versetzt, färbt sich beim Durchleiten von Cyangas allmählig dunkel. Unterbricht man das Einleiten sobald die Flüssigkeit weinroth geworden, und lässt sie unge-fähr 16 Stunden verschlossen stehen, so ist sie noch bedeutend nachgedunkelt und der Geruch des Cyans demjenigen der Blausäure gewichen. Zuweilen haben setzen sich auch schwarze Krusten an den Wänden des Gefäßes ab. Von diesen wird abfiltrirt, der Aether bei möglichst niedriger Tempera-tur verdunstet und der klebrige, braune Rückstand mit kaltem, verdünnten Alkohol vom färbenden Harze befreit. Das verbleibende, weisse, krystallinische Pulver, welches zwischen Filtrirpapier möglichst abgepresst und über

<sup>1</sup> Hofmann, *Annalen*, 66, 129 (1848).

Schwefelsäure getrocknet wird, löst sich sehr schwer in kaltem Aether und Benzol. Es lässt sich nicht umkristallisieren, da es beim Erhitzen in Lösungsmitteln rasch verharzt; mit Alkohol benetzt, zersetzt es sich sogar schon an der Luft. In reinem Zustande schmilzt es unter Zersetzung bei  $165^{\circ}$ , wird jedoch schon gegen  $120^{\circ}$  violett und dann braun. Aus 5 gr des Amidins lassen sich 3 gr des Produktes erhalten.

Aus der Elementaranalyse ergibt sich für den Körper eine Zusammensetzung  $C_{16}H_{16}N_4O$ .

- I. 0.2169 gr Substanz gaben 0.5409 gr  $CO_2$  und 0.1023 gr  $H_2O$ .
- II. 0.2625 gr Substanz gaben 0.6596 gr  $CO_2$  und 0.1380 gr  $H_2O$ . [46]
- III. 0.2060 gr Substanz gaben 0.5184 gr  $CO_2$  und 0.1152 gr  $H_2O$ .
- IV. 0.3659 gr Substanz gaben 63.75 ccm N,  $t=25^{\circ}$ ,  $B_0=760.5$  mm,  $\tau=18.4$  mm.
- V. 0.1498 gr Substanz gaben 27.2 ccm N,  $t=24^{\circ}$ ,  $B_0=765.5$  mm,  $\tau=17.34$ .

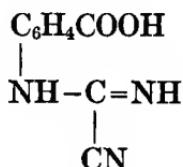
	Berechnet für:		Gefunden:					
	$C_{16}H_{16}N_4O$		I	II	III	IV	V	Mittel
C	192	68.57	68.00	68.52	68.60	—	—	68.37
H	16	5.71	5.24	5.84	6.21	—	—	5.76
N	56	20.00	—	—	—	19.55	20.32	19.94
O	16	5.71	—	—	—	—	—	5.93
	280	99.99						

Da der Sauerstoffgehalt wahrscheinlich, analog mehreren ähnlichen Cyanderivaten, vom Krystallwasser herführt, lässt sich diese Bruttoformel auflösen:—

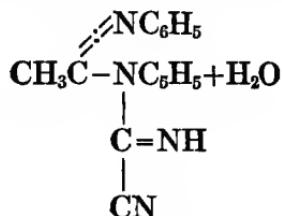


Es hat somit die Reaktion nicht den Verlauf genommen welchen Hofmann beobachtet hat, die Anlagerung eines Cyan-

moleküls an je zwei primäre oder sekundäre Amingruppen. Viel eher folgt das Amidin hierin der Amidobenzoësäure, dass sich ein ganzes Cyanmolekül an eine einzelne ersetzbaren Wasserstoff enthaltende Stickstoffgruppe anlagert. Da nach Griess<sup>1</sup> aus der Amidobenzoësäure die Cyancarbimidoamidobenzoësäure entsteht —



so liesse sich der neue Körper nach demselben Schema —



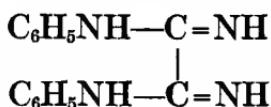
[47] schreiben und kann ich diese als die wahrscheinlichste Konstitutionsformel aufstellen.

Der Körper erleidet beim Erhitzen mit Wasser unter Druck eine Umwandlung in einen rothen Farbstoff, welcher in Chloroform löslich, aber nicht krystallisirbar ist und daher nicht weiter untersucht wurde. Zugleich tritt ein starker Isonitrilgeruch auf.

Mineralsäuren zersetzen die Substanz vollkommen, so dass Anilin und Essigsäure die hauptsächlichsten Produkte sind. Wenn man dagegen das C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O in ganz kleinen Portionen in siedende starke Kalilauge einträgt, so löst es sich darin auf, unter Abscheidung von viel Anilin. Nachdem letzteres durch andauerndes Kochen entfernt ist, setzen sich beim

<sup>1</sup> Griess, *Berichte*, 11, 1985 (1878).

Erkalten flimmernde Krystallblättchen ab. Die abfiltrirte Flüssigkeit enthält Essigsäure, Kohlensäure, Oxalsäure und Blausäure; die ausgeschiedenen Krystalle sind in Benzol und Aether nicht, in heissem Alkohol nur sehr sparsam löslich, leicht dagegen in heißer und verdünnter Salzsäure. Auf Alkalizusatz fällt ein flockiger weisser Niederschlag aus, der zur Reinigung einmal aus Alkohol umkrystallisiert wird. Weisse, silberglänzende Blättchen, die bei 214° schmelzen und sich beim vorsichtigen Erhitzen zwischen Uhrgläsern zum Theil sublimiren lassen. Dies Alles gab dem Zersetzungsprakt den Anschein als wäre es das Hofmann'sche Cyananilin<sup>1</sup>



und eine Analyse hat die Vermuthung in der That bestätigt: 0.2076 gr der getrockneten Substanz gaben 42 ccm N, t=17.5°, B<sub>0</sub>=764.7, τ=11.6.

Verlangt für:



N 23.53

Gefunden:

23.63 Procent.

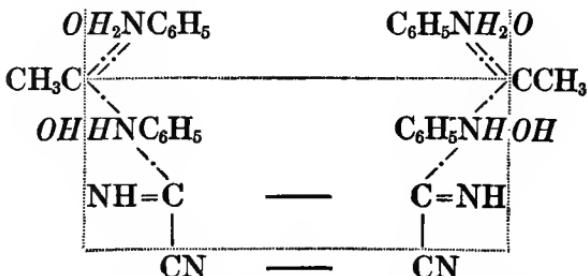
[48] 5 Gramm C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O haben 1.5 Gramm Cyananilin geliefert, welches Gewicht der Hälfte der in ersterem enthaltenen Anilinreste entspricht. Es kann also nicht bezweifelt werden dass der Einfluss der Kalilauge folgender war —



Wenn diese glatte Spaltung auch nicht als strenger Beweis für die oben aufgestellte Konstitution des Körpers C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O gelten kann, so betrachte ich sie dennoch als wesentliche

<sup>1</sup> Hofmann, *Annalen*, 66, 129 (1848).

Stütze derselben, da sie aus derselben ungezwungen hervorgeht.



Andere Umwandlungen mit dem Körper  $C_{16}H_{16}N_4O$  auszuführen ist mir nicht gelungen.

Ich habe nun noch einige andere Substanzen der Einwirkung des Phosgengases unterworfen und glaube, dass es einigen Werth hat über diese Versuche zu berichten, wenn dieselben auch nicht zur Auffindung noch unbekannter Derivate geführt haben.

#### EINWIRKUNG DES PHOSGENS AUF URETHAN

In der Hoffnung zu einem Carbonyldiurethan



zu gelangen, habe ich wiederholt 7 Teile Aethylurethans mit 1 Theil Phosgen, entweder verflüssigt oder in Benzol gelöst, im Rohr auf  $75^\circ$  erhitzt. Beim Oeffnen der Röhren entwichen jedesmal unter starkem Drucke Salzsäure und Chloräthyl, und es verblieb als Reaktionsprodukt eine [49] chlorfreie, in kaltem Wasser unlösliche Substanz. Dieselbe musste wiederholt aus Alkohol oder Chloroform umkristallisiert werden, bis sie bei  $194^\circ$  einen konstanten Schmelzpunkt erreichte. Sie wurde bei  $120^\circ$  getrocknet und analysirt, wobei es sich herausstellte, dass die Formel nicht die erwartete sondern  $C_4H_8N_2O_3$  sei.

- I. 0.2749 gr Substanz gaben 0.3703 gr CO<sub>2</sub>  
und 0.1549 gr H<sub>2</sub>O.
- II. 0.2986 gr Substanz gaben 55 ccm N, t=24°,  
 $B_0=759.4$  mm,  $\tau=17.34$  mm.
- III. 0.2105 gr Substanz gaben 38 ccm N, t=19°,  
 $B_0=764.45$  mm,  $\tau=12.72$  mm.

	Berechnet für:		Gefunden:		
	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>		I	II	III
C	48	36.36	36.12		
H	8	6.06	6.12		
N	28	21.21		20.73	20.94
O	48	36.36			
	132	99.99			

Es hatte sich somit Allophansäureester gebildet, der sich auch noch dadurch nachweisen liess, dass er sich durch Erhitzen mit Ammoniaklösung in das Biuret verwandelte. Ob sich nun dieser Ester direkt gebildet hat, nach der Gleichung



oder ob das zuerst entstandene Carbohydiurethan beim Umkrystallisiren zerfällt, vermag ich nicht zu entscheiden. Ich neige jedoch zu ersterer Ansicht.

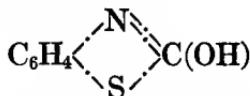
Versuche mit dem homologen Alanin führten zu keinem Resultat.

Ferner ergab sich aus wiederholten Versuchen die Unfähigkeit des Phosgen sich mit Carbazol, Succinimid oder Phthalimid, oder deren Kaliumderivaten zu verbinden.

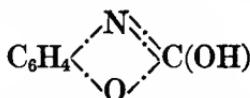
Auf Hydrazobenzol wirkt Phosgen wie eine Säure: daselbe verwandelt sich in Benzidin, welch' letzteres, wie schon [50] bekannt, erst bei hohen Temperaturen von Chlorkohlenoxyd angegriffen wird.

Auch mit Thioharnstoff wollte das Phosgen nicht in Wechselwirkung treten, obwohl die Versuche bei verschiedenen Temperaturen angestellt wurden. Selbst nach wochenlangem Zusammenstehen liess sich keine Veränderung erkennen.

Orthoamidophenylmerkaptan, welches ich der Güte des Herrn Professor Hofmann verdankte, reagirt sehr leicht mit Phosgen. Es wurde mit Benzol vermischt und tropfenweise mit Phosgenlösung versetzt, bis kein salzaures Salz mehr ausfiel. Hierbei wurde viel Hitze frei. Das Benzol enthielt einen chlorkreinen, sofort bei 136° konstant schmelzen den Körper, welcher unschwer als Hofmanns Oxymethenylverbindung zu erkennen war.



Schon Grönvik<sup>1</sup> hatte aus dem Orthoamidophenol mittels Chlorameisensäureesters den analogen Körper erhalten



Versuche, das Phosgen auch auf das Benzenylamidomerkaptan einwirken zu lassen, blieben erfolglos.

[51] Die im vorstehenden beschriebenen Versuche habe ich im Juli 1885 im I. Chemischen Laboratorium der Universität Berlin begonnen und im Januar 1887 beschlossen. Es ist mir eine grosse Freude an dieser Stelle bezeugen zu können wie viel ich meinen verehrten Lehrer, Herrn Geheimrath Professor Hofmann, für seine lebhafte Anregung, Belehrung und Unterstützung schulde und mit welcher Dankbarkeit

<sup>1</sup> *Bull. Soc. Chim. n. s. 25, 177 (1876).*

ich mich immer des Wohlwollens erinnern werde, das er mir stets gezeigt.

Auch Herrn Professor Gabriel sage ich für viele freundliche Rathschläge meinen herzlichsten Dank.

OPPONENTEN:<sup>1</sup>

Die Herren: W. Bowman, Cand. phil.  
K. Auwers, Dr. phil.  
A. Reissert, Dr. phil.

THESEN.

I.

Die vier Bindungseinheiten des Kohlenstoffs sind unter einander gleichwerthig.

II.

Die einfach-substituirten Thioharnstoffe sind Derivate des Thioharnstoffes.

III.

Die Clausius'sche Theorie ist die beste Erklärung der elektrolytische Vorgänge.

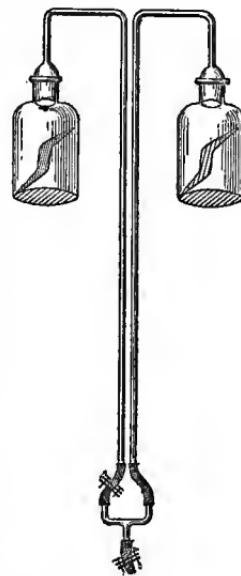
<sup>1</sup> In the public examination for the Doctor's degree, Morris Loeb defended the accompanying theses against the three opponents here named. [EDITOR.]

## THE MOLECULAR WEIGHT OF IODINE IN ITS SOLUTIONS<sup>1</sup>

IT is a matter of everyday observation that iodine has the property of dissolving with different colors in different liquids; in some it shows the reddish-brown hues of its solid and liquid states; in others it acquires the violet color so characteristic of its vapor. The inference seems very natural that this diversity of color must depend on a different form of aggregation of the iodine atoms within the solvent. Since the molecules of solids and liquids appear to be more complex than those of gases, we might suppose that the red solutions contain more complex molecules of iodine than do the violet ones. This is, in fact, the usual assumption; but apart from certain qualitative indications, there has been no proof of its truth; quantitative evidence has not yet been forthcoming in support of the hypothesis. That I have been fortunate in obtaining such, I owe to those new [806] means of investigating the state of dissolved matter with which the happy generalizations of Raoult, and the skillful mathematical deductions of van't Hoff, have furnished us. I refer to the phenomena of "osmotic pressure," which can be measured by the depression of freezing-point and vapor tension which liquids experience when mingled with a foreign substance. By the advice of Professor Ostwald, I undertook to attack the problem of the molecular weight of iodine in its solutions by the vapor-tension method, and I now give the results of the experiments carried out under his direction at the Chemico-Physical Laboratory of Leipzig University.

<sup>1</sup> Reprinted from the *Journal of the Chemical Society*, **53**, 805 (October, 1888).

Two liquids at once presented themselves as the appropriate solvents, ether and carbon bisulphide; they both have a considerable vapor tension, and they may be considered as typical of the two kinds of solvents for iodine. For, whereas many iodine solutions show impure tints, that in ether is of a deep reddish-brown, and that in carbon bisulphide of a pure violet. It was not so easy to find a proper apparatus, as Raoult's is quite inapplicable. He operates in the Torricellian vacuum, and has merely to note the comparative heights of the mercury when the solution and the pure solvent are introduced above it. In the case of iodine, all contact with mercury must obviously be avoided. After various attempts, the following apparatus was devised, which is an adaptation of Regnault's manometer to the [807] present purpose. It consists of two bottles of nearly equal capacity, provided with carefully ground, hollow glass stoppers. To these stoppers, glass tubes are adapted, 60 cm. long, and of about 6 mm. bore, which are bent twice at right angles, so that there is an ascending limb and a horizontal piece of 10 cm. length each, and a descending limb, 40 cm. long, for each half of the apparatus. The lower ends of these two tubes are connected with each other by means of a T-tube, to which they are joined by short pieces of very stout rubber tubing; the third end of the T-tube serves as a communication with the exterior when needed, and carries a rubber tube with pinchcock. The communication between the two halves of the apparatus can also be interrupted by means of a pinch-cock on one of the rubber joints. In one



of the bottles, the iodine solution is placed, whilst the pure solvent is put into the other. These liquids are contained in glass tubes, drawn out at both ends into capillaries that make an obtuse angle with the wider part. The tubes are first weighed, then filled, closed before the blowpipe, and again weighed. They contain about 3 cc. of liquid, pass readily through the narrow necks of the bottles, and can be broken by moderately shaking the bottles. Before this is done, however, the bottles are closed with their stoppers—smeared with deliquesced phosphoric acid to insure a perfect joint—and are placed in a water-bath of constant temperature. The T-tube is now connected with a two-necked Woulff's bottle, filled with colored distilled water, and communicating by its second neck with an air-pump. Air is exhausted, until the pressure within the apparatus is diminished to an extent equivalent to the amount of tension to be expected from the vapors of the liquids, and the pinch-cock is then closed, so as to interrupt communication with the Woulff's bottle. The air-pump being disconnected, atmospheric pressure is restored in the Woulff's bottle, and on carefully opening the pinch-cock the water is allowed to ascend halfway up the long tubes; the pinch-cock is then closed, and the Woulff's bottle removed. The apparatus is thus converted into a very delicate differential manometer, affording direct readings of the difference of pressure in the two bottles in terms of water centimetres; for convenience, the two tubes are brought closely together (see figure) and a scale is placed behind them.

The apparatus is quite independent of changes in the atmospheric pressure; the change in capacity, caused on either side by an alteration in the level of the water in the tubes, is, moreover, so slight in proportion to the volume of air in the bottles, that it can safely be neglected; the effect of capillarity in the two tubes is equal and opposite, so that this too may

be left out of account. There remains only the effect of the air left in the apparatus by the air-pump. It [808] is obvious that equilibrium being once established, and the temperature in all parts remaining the same, the pressure of the air in the one half will always counterbalance that in the other. In fact, partial exhaustion was only resorted to as a means of preventing too great an outward pressure during the course of the experiment, since it was difficult to prevent leakage where there was any outward pressure upon the stoppers. Partial exhaustion, besides obviating this difficulty, proved directly advantageous by promoting a more rapid diffusion of the vapors, and thereby shortening the duration of the observations.

The apparatus having been made ready, communication between the two halves was temporarily interrupted, and the tubes containing the liquids broken by shaking the two bottles simultaneously. After ten to fifteen minutes communication was restored, and now the level of the water in the two manometer tubes, equal before, was seen to differ considerably, indicating a higher pressure in the bottle containing the pure solvent. Readings being made from time to time, this difference of level sometimes appeared virtually constant for hours, whilst in other cases it would exhibit considerable variations, which I ascribe to slight inequalities of temperature and to the unequal concentration of the solution in different parts of its bottle. After standing twenty-four hours, the aqueous vapor from the manometer tubes generally began to diffuse into the bottles, and by moistening the ether or carbon bisulphide rendered further observations useless.

The readings give the difference between the vapor tension of the pure solvent and that of the solution; that is, the depression of tension which corresponds with the proportion of iodine to solvent in the solution. To calculate the con-

centration of the solution at the moment of observation, I required two data: the amount of iodine and of solvent introduced into the bottle (which I obtained from the weighings of the sealed tubes and from the known strength of the solution with which they were filled); and secondly, the amount of solvent which had assumed the gaseous state, and must therefore be deducted from the original quantity in solution. This was easily calculated by the regular gasometric formula, the volume of gas being 270 cc., the temperature being known, and the pressure being that of the vapor of the pure solvent, less the depression formed by the direct observation. I found that I could employ the vapor tensions of pure ether and carbon bisulphide from tables calculated from Regnault's measurements, as a few direct comparisons proved that they agreed with those given by my apparatus, within the limits of experimental error. The expression for the amount of solvent remaining in the solution at the moment of observation is therefore —

$$[809] \quad a - \frac{270 \cdot w(f-e)}{760(1+at)}$$

where  $a$  = grams of solvent originally present;  $f$  = the tension at the temperature  $t$  of the pure solvent, expressed in millimetres of mercury;  $e$  = the depression of tension, also in terms of millimetres of mercury;  $w$  = weight in grams of 1 cc. of the vapor under standard conditions. Now if  $b$  = the weight of iodine in the solution, and  $p$  = the ratio of solvent to iodine —

$$\text{I.} \quad p = \frac{b}{a - \frac{270 \cdot w \cdot (f-e)}{760 \cdot (1+at)}}$$

The concentration being thus ascertained, the calculation of the molecular weight of iodine was made according to the formula —

II.

$$M_1 = M_0 \frac{p(f-e)}{e}$$

$M_1$  and  $M_0$  being the molecular weights of iodine and solvent respectively. This is a working formula derived by Raoult from an expression for the relation between the ratio of molecules of solvent and substance dissolved on the one hand, and the ratio between the tension of the pure solvent and the depressed tension on the other, where the dissolved substance itself has a comparatively insignificant tension. It is interesting to note that the latter expression was reached independently and almost simultaneously by Planck.<sup>1</sup>

In the following tabulated statement of my observations, the first two columns show the weights of the ingredients of the solution originally introduced; the third gives the temperature; the fourth, the depression of tension; the fifth, the true tension of the solution; the sixth, the concentration as calculated by formula I; finally, we have the molecular weight as calculated by formula II. Before giving the results obtained for iodine, I think it useful to give a summary of a few test experiments made on the molecular weight of naphthalene, which not only proved the trustworthiness of the method, but also showed that there is no specific difference between ether and carbon bisulphide which could invalidate the effect of the great difference of the molecular weights found for iodine.

<sup>1</sup> Compare Raoult, *Zeitschr. physik. Chem.* 2, 372 (1889), and Planck, *ibid.* 2, 408 (1888). [EDITOR.]

## [810] NAPHTHALENE IN CARBON BISULPHIDE

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Average
5.4082	0.2586	27.5°	9.47	377.09	5.18	129	
—	—	27.5	10.93	375.65	5.18	135	{ 132

## NAPHTHALENE IN ETHYL ETHER

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Average
2.8359	0.1462	27.5°	21.12	557.27	6.53	127	
—	—	27.5	21.08	557.31	6.53	128	
—	—	27.5	21.14	557.25	6.53	127	
—	—	27.5	21.17	557.22	6.53	128	{ 127.5

Average in CS<sub>2</sub> ..... M<sub>1</sub> = 132Average in C<sub>4</sub>H<sub>10</sub>O ..... M<sub>1</sub> = 127.5Theory for C<sub>10</sub>H<sub>8</sub> ..... M<sub>1</sub> = 128.

## IODINE IN CARBON BISULPHIDE

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Average
5.6528	0.4388	27.3°	9.72	373.92	8.37	239	
—	—	27.3	8.59	375.05	8.37	278	
—	—	27.3	8.81	374.83	8.37	271	
—	—	27.3	9.08	374.56	8.37	268	{ 264
5.1862	0.4026	27.5	8.10	378.48	8.46	300.5	
—	—	27.5	8.10	378.48	8.46	300.5	{ 300.5
5.4579	0.2594	27.5	4.60	381.98	5.15	324	
—	—	27.5	4.51	382.07	5.15	332	
—	—	27.5	4.66	381.92	5.15	320	
—	—	27.5	4.76	381.82	5.15	314	
—	—	27.55	4.80	382.52	5.15	310	{ 320
4.9030	0.2330	27.5	4.67	381.91	5.20	326	
—	—	27.5	4.60	381.98	5.20	327	{ 326.5

Total average ..... M<sub>1</sub> = 303.25 ± 5.10Theory for I<sub>2</sub> ..... M<sub>1</sub> = 254Theory for I<sub>3</sub> ..... M<sub>1</sub> = 381.

[811]

## IODINE IN ETHYL ETHER

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f</i> - <i>e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Average.
8.2578	0.2546	27.2°	8.20	563.69	9.59	488	504.7
-	-	27.2	7.50	564.99	9.59	534	
-	-	27.2	7.81	564.08	9.59	512	
-	-	27.35	8.09	567.05	9.60	497	
-	-	27.3	8.16	565.90	9.60	492.5	
8.2864	0.2058	27.3	7.46	566.60	7.68	443	577.2
-	-	27.3	4.84	569.22	7.68	653	
-	-	27.3	5.04	569.02	7.68	642	
-	-	27.3	5.66	568.40	7.68	571	
8.6809	0.2305	27.4	6.51	569.72	7.50	486.5	480.7
-	-	27.4	6.48	569.75	7.50	487	
-	-	27.45	6.77	570.54	7.51	468.5	
8.4343	0.8151	27.5	6.99	571.40	7.62	461	466.1
-	-	27.5	7.14	571.25	7.62	451	
-	-	27.5	6.43	571.96	7.62	501.5	
-	-	27.5	7.14	571.25	7.62	451	

Total average .....  $M_1 = 507.2 \pm 10.5$ Theory for  $I_4$  .....  $M_1 = 508$ .

It seems very probable, therefore, that iodine in its red solutions has a molecular weight corresponding to  $I_4$ , whilst in the violet solution in carbon bisulphide there is a less complex aggregation, giving a value between  $I_2$  and  $I_3$ . I may as well remark that the values for *p* in the ether solutions correspond approximately with the ratio of one iodine molecule in 100 molecules of the solutions; in the carbon bisulphide solutions, this ratio varies between 1 : 100 and 1 : 200. Whilst greater dilution might appear more advisable from a theoretical point of view, it offers an apparently insurmountable difficulty in practice. A glance at the formulæ used in the calculation shows that the value of *e* enters three times in such a manner that any error attached to it would be tripled. As *e* decreases with the concentration, it is evident that a greater dilution than that employed by me will soon bring *e* to a point where

the chance errors of observation become proportionately very great. Hence I agree with Raoult when he says that the method of determining molecular weights by the depression of the freezing-point is preferable to the method by vapor tensions. But for the problem which immediately interested me I lacked a liquid which would solidify, and also dissolve iodine with a pure violet color, benzene, for instance, giving a very [812] impure bluish-brown. Nevertheless I endeavored to obtain what corroborative evidence I could by experimenting on the freezing points of iodine in acetic acid and in benzene, but was forced to give up the attempt by the very slight solubility of iodine in these menstrua at low temperatures; the molecular weight of iodine as calculated from various series of observations seemed to increase continuously with the concentration, so that there was no point in the narrow limits between extreme dilution and saturation at which the molecular weight would appear constant, and could be accepted as trustworthy. A paper published since then by Paternò and Nasini<sup>1</sup> on this subject contains a few figures for the molecular weight of iodine in acetic acid and benzene solutions, but I am unable to draw any other inference from them than from my own.

<sup>1</sup> *Berichte*, **21**, 2155 (1888).

[606] UEBER DEN MOLEKULARZUSTAND DES  
GELOESTEN JODS<sup>1</sup>

DAS Jod löst sich bekanntlich in Schwefelkohlenstoff und Kohlenwasserstoffen mit violetter Farbe, in Alkohol, Aether und andern Alkoholderivaten dagegen rotbraun auf, einerseits seiner Dampfform, andererseits seinem festen Zustande entsprechend. Man folgert gewöhnlich daraus, dass das Jod diese Zustände in den Lösungen behielte, oder, genauer gesprochen, dass die rote Farbe komplexere Molekel<sup>2</sup> andeutet als die violette. Eine quantitative Stütze dieser Annahme hat sich meines Wissens bisher nicht erforschen lassen; qualitativ allerdings sprechen Analogien in den Absorptionspektren dafür, sowie eine Beobachtung E. Wiedemanns,<sup>3</sup> wonach eine Lösung von Jod in Schwefelkohlenstoff bei starker Abkühlung aus violett in rotbraun übergeht. In der That wird die erste versprechende Aussicht auf Beantwortung derartiger Fragen über die Elemente durch jene Beziehungen eröffnet, welche neuerdings Raoult zwischen den Molekularzuständen einerseits und Änderungen in der Dampftension und dem Gefrierpunkte des Lösungsmittels andererseits hervorgehoben, und van 't Hoff mathematisch hergeleitet hat. Auf Veranlassung Herrn Professor Ostwalds habe ich nun Versuche angestellt, um zu erfahren, ob sich wirklich eine Verschiedenheit des Molekulargewichts des Jods in seinen Lösungen aus den Dampfdruckerniedrigungen derselben ergibt: ich glaube dies jetzt entschieden bejahen zu können.

Die Wahl des Lösungsmittels war nicht schwer, da Aether

<sup>1</sup> Reprinted from *Zeitschrift für physikalische Chemie*, 2, 606 (1888).

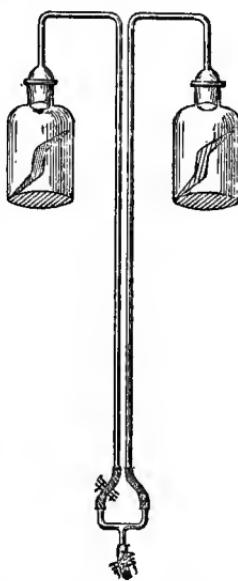
<sup>2</sup> This now almost obsolete spelling was generally used in 1888. [EDITOR.]

<sup>3</sup> *Phys.-Med. Gesell.* Erlangen (1887).

und Schwefelkohlenstoff, welche beide sehr hohe Dampfspannung besitzen, den Farbenunterschied in besonders schöner Weise zeigen und daher für typisch gelten können, während viele andere Lösungsmittel, wie Benzol, die unreinen Nuancen eines Uebergangszustandes hervorbringen. Dagegen liess sich die Raoult'sche Methode, die Lösungen in die Barometerleere einzuführen und den Quecksilberstand direkt zu messen, deshalb nicht anwenden, weil [607] eine Berührung zwischen Jod und Quecksilber nicht statthaft war. Es hat sich indessen eine Modifikation eines Regnault'schen Apparates als nützlich erwiesen, welche eine bequemere Handhabung und raschere Ausführung gestattet, genaue Messinstrumente unnötig macht und, trotz einiger neuen Fehlerquellen, hinreichende Genauigkeit besitzt, Fragen wie die vorliegende zu entscheiden.

Zwei Reagensflaschen von annähernd gleichem Gehalt erhalten guteingeschliffene, hohle Glasstöpsel, welche beiderseits offen sich nach oben in Glasröhren aus starkem Glase, von etwa 6 mm. lichter Weite, fortsetzen. Diese Röhren werden zweimal rechtwinklig gebogen, so dass der unten offene Schenkel 50 cm. lang ist, während der andere Schenkel und der wagrechte Teil nur je etwa 105 cm. lang sind. Diese beiden Röhren werden untereinander durch Stücke dicken Gummischlauchs, deren eines einen Quetschhahn führt, unter Vermittelung eines T-Rohres verbunden. Das dritte Ende dieses T-Rohres, — zweckmässig nach oben gekehrt, statt wie der Uebersichtlichkeit halber gezeichnet, — dient zur Verbindung nach aussen und ist deshalb mit Schlauch und Quetschhahn versehen. Es werden nun die Flaschen mit den die Flüssigkeiten enthaltenden Röhrchen beschickt, welche aus oben und unten stumpfwinklig ausgezogenen dünnwandigen Glasröhren gefertigt sind, 2 bis 3 cc. fassen und nach dem Füllen vor der Stichflamme geschlossen wer-

den. In die eine Flasche kommt die Lösung, in die andere das reine Lösungsmittel: die Flaschen werden geschlossen, nachdem noch zu besserer Dichtung die Stöpsel mit syrupsdicker Phosphorsäurelösung bestrichen worden. Das offene Ende der T-Röhre wird mit einem Rohre verbunden, das auf den Boden einer Woulff'schen Flasche reicht, welche mit gefärbtem Wasser gefüllt ist und mittels ihrer anderen Mündung mit einer Luftpumpe kommuniziert. Die Luft im Apparate wird so lange verdünnt, bis der Unterdruck den zu erwartenden höchsten Druck um wenigstens übertrifft, der Quetschhahn alsdann geschlossen und die Woulff'sche Flasche mit der Aussenluft in Verbindung gesetzt. Durch vorsichtiges Oeffnen des Hahnes lässt man nun so viel Wasser in die Röhren treten, dass dasselbe die Hälfte der langen Schenkel erfüllt. Man entfernt die Woulff'sche Flasche und hat nun ein empfindliches [608] Differentialmanometer, welches Druckunterschiede in Wasserhöhe direkt angibt, vom äusseren Druck ganz unabhängig ist und wegen der verschwindenden Verschiebung der Volume in beiden Hälften (die grösste beobachtete Differenz bedingte kaum einen halben cc., während die Flaschen 270 cc. fassen) hierfür eine Korrektion unnötig machte. Der Kapillaritätseinfluss hebt sich gegenseitig auf und die im Apparate verbleibende Luft übt auf beiden Seiten gleichen Druck aus, so dass ein Verdünnen derselben bloss zum Vermeiden eines grossen Druckunterschiedes zwischen dem Innern des Apparates und der Atmosphäre, wodurch bei längerem Stehen ein Austreiben der Stöpsel und folgliche Undichtigkeit häufig vorkam, nötig war. Es



ergab sich aber auch der weitere Vorteil, dass eine schnelle Verbreitung des Dampfes ermöglicht ward, wodurch die Dauer der Versuche eine kürzere wurde. Der Versuch wurde folgendermassen fortgeföhrt: die Flaschen wurden dicht zusammen in einen Wasserthermostaten bis an den oberen Rand des Halses gesteckt, während die beiden Manometerröhren ausserhalb desselben ebenfalls dicht beisammen herabhangen. Nachdem an einer lotrecht daneben hängenden Skala mit Millimeterteilung die kleine Niveaudifferenz festgestellt, wurde die Verbindung der beiden Hälften mittels des hierzu angebrachten Quetschhahns aufgehoben und die Röhrchen durch Schütteln der Flaschen geöffnet. Es dauerte eine Viertelstunde ehe man die Verbindung wieder herstellen durfte, ohne ein Ueberspritzen der Sperrflüssigkeit in die eine oder die andere Flasche befürchten zu müssen; dann aber stellte sich rasch ein Gleichgewichtszustand her, der manchmal viele Stunden lang unverändert blieb, manchmal aber um Centimeter Wasserdruk schwankte. Die Ursache des Schwankens lag wohl in ungleichmässiger Verteilung der Lösung in der Flasche und an kleinen Temperaturschwankungen, welche die Witterung der letzten Wochen sehr begünstigte. Nach eintätigigem Stehen war kein Vertrauen mehr in die Werte zu setzen, da alsdann die Diffusion des Wasserdampfes bis zur Flasche vorgeschritten war, die Flüssigkeiten nicht mehr trocken waren.

Die nun mit Rücksicht auf die ursprüngliche Differenz korrigierten Unterschiede des Wasserstandes ergaben also den Unterschied zwischen der Spannung des reinen Lösungsmittels und der jeweiligen Lösung; d. i. die Erniedrigung, welche die gerade in der Lösung bestehende Konzentration des Jods bewirkte. Zur Berechnung dieser Konzentration brauchte ich zweierlei Daten: die Mengen des thatsächlich vorhandenen Jods und Lösungsmittels, und die Menge des

letzteren, welches in Gasform der Lösung sich entzogen hatte. Die Röhrchen enthielten deshalb gewogene Mengen der einer frisch bereiteten Mischung der abgewogenen Bestandteile entnommenen [609] Lösung. Andererseits liess sich die verdampfte Menge des Lösungsmittels nach bekanntem gasometrischen Gesetze berechnen, wenn man nur den Druck, unter welchem dasselbe stand, kannte: derselbe ist gleich dem der reinen Flüssigkeit, vermindert um die abgelesene Erniedrigung. Wie ich mich durch direkte Versuche überzeugte, genügen die durch Interpolation aus den Regnaultschen Zahlen erhaltenen Werte für die reinen Flüssigkeiten vollkommen den Ansprüchen meiner Versuche. Es sei nun  $p$  das Verhältnis des in der Flüssigkeit augenblicklich vorhandenen Lösungsmittels zu dem darin aufgelösten Jod;  $a$  die eingewogene Menge des Lösungsmittels in Gramm ausgedrückt,  $b$  die des Jods;  $f$  der berechnete Quecksilberdruck des Gases über der reinen Flüssigkeit,  $e$  die gefundene Erniedrigung gleichfalls in Millimeter Quecksilberhöhe ausgedrückt;  $g$  das Gewicht eines Kubikcentimeters des Dampfes bei  $0^\circ$  und 760 mm. Dann haben wir, das Volum der Flasche gleich 270 cc. gesetzt, für das Gewicht des in dem flüssigen Teil verbliebenen Lösungsmittels den Ausdruck

$$a - \frac{270 \cdot g \cdot (f-e)}{760 \cdot (1+at)}$$

und daher

$$\text{I. } p = \frac{b}{a - \frac{270g(f-e)}{760(1+at)}}$$

Der weiteren Berechnung lege ich eine Formel zu Grunde, welche Raoult<sup>1</sup> jüngst aufgestellt hat, die ihrerseits auf dem

<sup>1</sup> Zeitschr. 2, 372 (1888).

von ihm und Planck<sup>1</sup> übereinstimmend gefundenen Gesetz für die Lösungen wenigflüchtiger Substanzen beruht. Diese Formel lautet

$$\text{II. } M_1 = M_0 \frac{p \cdot (f-e)}{e}$$

wobei  $M_0$  das Molekulargewicht des Lösungsmittels,  $M_1$  dasjenige des gelösten Körpers bedeutet. In den tabellarischen Zusammenstellungen meiner Versuche gebe ich, behufs besserer Uebersicht, in den beiden ersten Kolumnen die Gewichte der Ingredienzen der eingeführten Lösung, in der dritten die Temperaturen, in der vierten die gefundene Erniedrigung in Millimeter Quecksilber, in der fünften den berechneten Dampfdruck der Lösung, in der sechsten die Werte für  $p$  und endlich das sich ergebende Molekulargewicht des Jods. Zur Beurteilung der Methode mögen die Messungen dienen, welche ich an einem Körper von zweifellos konstantem [610] Molekulargewicht, dem Naphthalin, ausgeführt: ich schicke dieselben deshalb voraus.

#### NAPHTHALIN IN SCHWEFELKOHLENSTOFF

$a$	$b$	$t$	$e$	$f-e$	$p$	$M^1$
5·4082	0·2586	27·5°	9·47	377·09	5·18	129
—	—	27·5	10·93	375·65	5·18	135

Mittel der gefundenen Werte 132.  
Berechnet für  $C_{10}H_8$  128.

<sup>1</sup> *Zeitschr.* 2, 408 (1888).

## NAPHTHALIN IN AETHER

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Mittelwert
2.5990	0.2511	27.5°	32.84	535.55	12.47	150 <sup>1</sup>	
2.8859	0.1462	27.5	21.12	557.27	6.53	127	
—	—	27.5	21.08	557.31	6.53	128	
—	—	27.5	21.14	557.25	6.53	127	
—	—	27.5	21.17	557.22	6.53	128	ber. 128

## JOD IN SCHWEFELKOHLENSTOFF

<i>a</i>	<i>b</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M</i> <sub>1</sub>	Mittel
5.6528	0.4388	27.3°	9.72	373.92	8.37	239	
—	—	27.3	8.59	375.05	8.37	278	
—	—	27.3	8.81	374.83	8.37	271	
—	—	27.3	9.08	374.56	8.37	268	
5.1862	0.4026	27.5	8.10	378.48	8.46	300.5	300.5
—	—	27.5	8.10	378.48	8.46	300.5	
5.4579	0.2594	27.5	4.60	381.98	5.15	324	
—	—	27.5	4.51	382.07	5.15	332	
—	—	27.5	4.66	381.92	5.15	320	
—	—	27.5	4.76	381.82	5.15	314	
—	—	27.55	4.80	382.52	5.15	310	
4.9030	0.2330	27.5	4.67	381.91	5.20	326	326.5
—	—	27.5	4.60	381.98	5.20	327	

Mittelwert aller Versuche  $M_1 = 303.25 \pm 5 \cdot 10^2$ Berechnet für  $I_2$ ,  $M_1 = 254$ ." "  $I_3$ ,  $M_1 = 381$ .

<sup>1</sup> Dieser Versuch war mit zu konzentrierter Lösung angestellt, um in Betracht zu kommen.

<sup>2</sup> Der wahrscheinliche Fehler ist nach der Formel  $F = \pm \sqrt{\frac{f_1^2 + f_2^2 + \dots + f_n^2}{n(n-1)}}$  berechnet. Der mittlere wahrscheinliche Versuchsfehler beträgt 19.

## [611] JOD IN AETHER

<i>a</i>	<i>c</i>	<i>t</i>	<i>e</i>	<i>f-e</i>	<i>p</i>	<i>M<sub>1</sub></i>	Mittel
3·2578	0·2546	27·2°	8·20	563·69	9·59	488	
—	—	27·2	7·50	564·39	9·59	534	
—	—	27·2	7·81	564·08	9·59	512	504·7
—	—	27·35	8·09	567·05	9·60	497	
—	—	27·3	8·16	565·90	9·60	492·5	
3·2864	0·2058	27·3	7·46	566·60	7·68	448	
—	—	27·3	4·84	569·22	7·68	658	577·2
—	—	27·3	5·04	569·02	7·68	642	
—	—	27·3	5·66	568·40	7·68	571	
3·6809	0·2305	27·4	6·51	569·72	7·50	486·5	
—	—	27·4	6·48	569·75	7·50	487	480·7
—	—	27·45	6·77	570·54	7·51	468·5	
3·4843	0·3151	27·5	6·99	571·40	7·62	461	
—	—	27·5	7·14	571·25	7·62	451	466·1
—	—	27·5	6·43	571·96	7·62	501·5	
—	—	27·5	7·14	571·25	7·62	451	

Mittel aller Versuche  $M_1 = 507\cdot2 \pm 10\cdot5$ .

Wahrscheinlicher Fehler eines Versuchs = 42.

Berechnet für  $I_4$ ,  $M_1 = 508$ .

Aus diesem Material ergiebt sich mit grosser Wahrscheinlichkeit, dass das Jod in roter Lösung ein der Formel  $I_4$  entsprechendes Molekulargewicht besitzt, während sich aus der Schwefelkohlenstofflösung ein halbwegs zwischen  $I_2$  und  $I_3$  stehender Wert berechnet. Um den Vergleich mit andern Berechnungsweisen zu erleichtern, mache ich noch darauf aufmerksam, dass meine Werte für  $p$  bei Aetherlösungen ungefähr einer Molekel  $I_4$  auf hundert Molekel des Gemenges entsprechen, während in den Schwefelkohlenstofflösungen das Verhältnis zwischen 1 : 100 und 2 : 100 schwankte. Dass sich grössere Verdünnungen bei dieser, sowie der Raoult'schen Versuchsordnung verbieten, wird klar, wenn man bedenkt, dass der Wert  $e$  in der Berechnung dreimal auftritt und man denselben daher nicht sich so verkleinern lassen darf, dass die

Beobachtungsfehler verhältnissmässig bedeutend werden. Es wäre daher, wie schon Raoult bemerkt, überhaupt die Gefrierpunktsmethode der Dampfspannungsmethode immer vorzuziehen. Um das mir vorgestckte Ziel zu erreichen, fehlte es mir aber vor allem an einem gefrierbaren Lösungsmittel, welches das Jod mit reinvioletter Farbe löste; Benzol giebt, wie schon erwähnt, eine Mischfarbe. Trotzdem habe ich im Verlaufe der Untersuchung Versuche über die Gefrierpunkte der Lösungen von Jod in Benzol sowohl, [612] wie in Eisessig angestellt. Ich gab dieselben aber auf, als ich mich überzeugt, dass bei der sehr geringen Löslichkeit des Jods in den erwähnten Flüssigkeiten ein genügender Spielraum nicht vorhanden ist: das berechnete Molekulargewicht nahm von der äussersten Verdünnung bis zur Sättigung stetig mit der Konzentration zu, so dass sich kein Punkt zeigte, bei welchem man einen Vorzug über die andern erkennen konnte. Die jüngst von den Herren Paternò und Nasini<sup>1</sup> veröffentlichten Zahlen scheinen mir Aehnliches zu ergeben.

Herrn Professor Ostwald freue ich mich für das liebenswürdige Interesse, welches er mir während dieser unter seiner Leitung ausgeführten Arbeit gezeigt, hier öffentlich danken zu dürfen.

<sup>1</sup> *Berichte*, 21, 2155 (1888).

## [812] THE USE OF ANILINE AS AN ABSORBENT OF CYANOGEN IN GAS ANALYSIS<sup>1</sup>

IN a paper published in the "Comptes Rendus," **100**, 1005, some time ago, Jaquemin proposed the use of aniline as an absorbent for cyanogen in quantitative gas analysis, without, however, giving details of any experiments as to the trustworthiness of the method. The proposal is a surprising one, considering that hydrogen cyanide is always formed in the preparation of cyananiline; this fact is distinctly stated by Hofmann,<sup>2</sup> who accounted for its production by certain secondary reactions which he studied. It is also to be noted that Jaquemin, in the same paper, describes a very satisfactory method of preparing cyanogen gas in the wet way, and that he probably employed the moist cyanogen in his experiments with aniline. As the presence of water seems to favor most of the reactions of cyanogen, there did not seem to be any conclusive evidence that dry cyanogen would be totally absorbed by aniline. At all events, it seemed worth while to make the experiment with cyanogen prepared in the old way, and at the same time to ascertain to what extent the development of hydrocyanic acid would interfere with Jaquemin's proposed method for gas analysis. For this purpose, cyanogen prepared from dry mercuric cyanide was brought into contact with recently distilled aniline. The gas was, indeed, absorbed rapidly and completely, nor did a bubble of gas appear after twenty-four hours' standing. But as soon as carbon dioxide was passed in, the presence [813] of hydrocyanic

<sup>1</sup> Reprinted from *Journal of the Chemical Society*, **53**, 812 (October, 1888).

<sup>2</sup> Hofmann, *Annalen*, **66**, 129 (1848).

acid became apparent. It was expelled from the aniline by the carbon dioxide, and could now be recognized both by its odor and by the Prussian blue reaction. At the same time a considerable quantity of carbon dioxide is absorbed by the aniline and must be held in solution, as chemical union is impossible under the circumstances. As the same is said to be the case with carbon monoxide, and these two gases are those which generally accompany cyanogen, I fail to see how aniline can be generally useful in determining the amount of cyanogen in a mixture, apart from the fact that hydrogen cyanide is produced in the reaction, and is itself very loosely attracted by aniline.

The experiments by which I satisfied myself of this were made last April, in the laboratory of the Physical Association of Frankfort-on-Main, to the director of which, Dr. B. Lepsius, I am very much indebted. The details of a few of the most important tests are given below.

I. 32·88 cc. of cyanogen gas (under standard conditions) were absorbed immediately by 12·5 cc. aniline; after twenty-five hours no trace of gas had been evolved.

II. A mixture of cyanogen and dry air was introduced into a T-shaped eudiometer, provided with stopcocks and filled with mercury. Aniline was first added and allowed to absorb the cyanogen, and dry carbon dioxide was then passed in; when no further change took place, the unabsorbed gas was transferred to a test-tube over mercury, and brought in contact with a few drops of sodic hydrate; the alkaline solution gave an appreciable test for hydrocyanic acid with ferrous and ferric salts. In the table [on the following page] the measurements and the results are given:—

	<i>t</i>	B	cc	Corrected	
Volume of cyanogen and air . .	19·0°	752·1	60	55·34	—
Volume 22 hours after introducing aniline . . . . .	19·5	752·1	7·7	7·09	—
Volume of cyanogen absorbed . .	—	—	—	—	48·25
After addition of carbon dioxide . .	19·5	752·1	36·75	33·84	—
Volume carbon dioxide . . . . .	—	—	—	—	26·75
After 23·5 hours . . . . .	19·5	752·0	21·00	19·33	—
Volume carbon dioxide absorbed . .	—	—	—	—	14·51

III. A similar experiment, performed in a somewhat different order, and with the use of a straight eudiometer, gave an analogous result. *H*=the height of the column of mercury, *h*=the height of the column of aniline reduced to mercury.

[814]

	<i>t</i>	B	<i>H</i>	<i>h</i>	cc	Corrected
Volume of carbon dioxide . . . .	19·5°	752·1	—	—	56·5	52·03
Volume of carbon dioxide and cyanogen . . . . .	19·5	752·1	—	—	108·5	99·91
Volume of cyanogen . . . . .	—	—	—	—	—	47·88
Vol. 22 hours after introduction of aniline . . . . .	19·5	752·0	227	5·3	43·0	27·32
Volume of gas absorbed . . . . .	—	—	—	—	—	72·59

47·88 cc. cyanogen gas and 24·71 cc. carbon dioxide have, therefore, been absorbed. In this case, too, the residual gas had a decided odor of prussic acid.

## [948] ZUR KINETIK DER IN LÖSUNG BEFINDLICHEN KÖRPER<sup>1</sup>

### 1. EINLEITUNG

BEKANNTLICH hat Herr Fr. Kohlrausch,<sup>2</sup> ausgehend von der Hittorf'schen Hypothese, wonach die Ueberführungszahl einer Lösung das Verhältnis der Geschwindigkeiten der beiden Jonen, in welche das in Lösung befindliche Salz zerfällt, berechnen lässt, zwischen dieser Grösse und dem elektrischen Leitungsvermögen eine einfache Beziehung aufgestellt. Hier-nach ist das Leitungsvermögen  $\lambda$  eine additive Eigenschaft, nämlich gleich der Summe der Beweglichkeiten des Anions  $v$  und des Kations  $u$ . Die Ueberführungszahl eines Jons ist das Verhältnis der Beweglichkeit dieses Jons zu der Summe der Beweglichkeiten der beiden Jonen. Es ist somit, wenn  $n$  die Ueberführungszahl des Anions, und somit  $1-n$  dieselbe Grösse für das Kation bedeutet: —

$$\lambda = u+v; \quad n = \frac{v}{u+v}; \quad 1-n = \frac{u}{u+v}.$$

Diese Beziehungen fand Herr Kohlrausch an einer Anzahl Verbindungen einbasischer Säuren sowie an einigen einwertigen Basen in Lösungen geringer Konzentrationen gut bestätigt; schwache Basen (z. B. Ammoniak) und Säuren (z. B. Essigsäure) fügten sich selbst bei beträchtlichen Verdünnungen auch nicht näherungsweise unter obige Gesetze.

Diesen Widerspruch zwischen Theorie und Erfahrung hat kürzlich Herr Arrhenius<sup>3</sup> durch Einführung des Aktivitätsbegriffes gehoben. Das Leitungsvermögen kann nur in dem

<sup>1</sup> In collaboration with W. Nernst. Reprinted from *Zeitschr.* **2**, 948 (1888).

<sup>2</sup> Fr. Kohlrausch, *Wied. Annalen*, **6**, 1 (1879). *Ibid.*, **26**, 213 (1885).

<sup>3</sup> Arrhenius, *Sur la conductibilité*, etc. Stockholm, 1884. *Zeitschr.* **1**, 631 (1887).

Falle eine additive Eigenschaft sein, wenn in allen Verbindungen die Jonen sich sämtlich oder mit einem [949] konstanten Bruchteil an der Leitung beteiligen. Nach der Theorie von Arrhenius ist dieses nicht der Fall. Die Elektrizitätsleitung wird nur von den aktiven Molekülen übernommen; der Aktivitätskoeffizient, d. h. das Verhältnis der leitenden zu den insgesamt vorhandenen Molekülen variiert nicht nur bei den verschiedenen Verbindungen, sondern er ist auch bei derselben Verbindung von der Konzentration abhängig, dergestalt, dass er mit der Verdünnung wächst und bei grosser Verdünnung dem Grenzwerte 1 zustrebt. Kohlrauschs Gesetz erlangt daher hiernach im allgemeinen erst bei sehr kleinen Konzentrationen strenge Gültigkeit. Die gute Uebereinstimmung, welche man l. c. S. 215<sup>1</sup> findet, röhrt daher, dass die daselbst aufgeföhrten Verbindungen bei der Konzentration  $\frac{1}{10}$  normal, auf welche sich die Leitungsvermögen und Ueberführungszahlen beziehen, einen nahe gleichen Aktivitätskoeffizienten, etwa 0.88, besitzen. Uebri gens sei darauf hingewiesen, dass auch Herr Kohlrausch selber<sup>2</sup> seinem Gesetze eine näherungsweise Gültigkeit zuschrieb und eine Untersuchung zur Prüfung desselben bei grossen Verdünnungen für wünschenswert hielt. Eine neuere Untersuchung von Herrn Ostwald,<sup>3</sup> in der die Leitvermögen einer grossen Anzahl Elektrolyte bis zu sehr bedeutenden Verdünnungen untersucht wurden, hat bereits ein diesen Anschauungen günstiges Resultat geliefert.

Den physikalischen Unterschiede zwischen den aktiven und inaktiven Molekülen hat Herr Arrhenius bekanntlich in Weiterführung der Clausius-Williamsonschen Hypothese darin gefunden, dass jene in ihre mit gleich grosser aber ent gegengesetzter Elektrizität geladene Jonen dissociert sind,

<sup>1</sup> Kohlrausch, *Wied. Annalen*, **26**, 215 (1885).

<sup>2</sup> *Loc. cit.* S. 216 (1885).

<sup>3</sup> Ostwald, *Zeitschr.* **1**, 61 und 97 (1887).

während bei letzteren der elektropositive und negative Bestandteil in ihrem Bewegungszustande nicht von einander unabhängig sind.

Um nun Kohlrauschs Gesetz von diesen veränderten Gesichtspunkten aus zu prüfen, fehlt es vor allem an genügenden Untersuchungen der Ueberführung, worüber in anbetracht der Wichtigkeit, welche die genaue Kenntnis dieses Phänomens für die Mechanik der Elektrolyse und die Konstitution der Lösungen besitzt, überraschend wenige Arbeiten vorliegen. Seit den klassischen Untersuchungen von Herrn Hittorf<sup>1</sup> haben nur vereinzelt Forscher<sup>2</sup> Messungen hierüber angestellt. In der Absicht, zur Ausfüllung dieser Lücke in der Wissenschaft beizutragen und eine Prüfung obigen Gesetzes an sehr verdünnten Lösungen zu ermöglichen, haben wir an einer Anzahl Säureradikale, hauptsächlich organischer Natur [950], durch, gleichzeitige Messungen der Ueberführung und der Leitfähigkeit von Silbersalzen die Jonenbeweglichkeiten zu ermitteln gesucht, deren Kenntniss, wie einer von uns zu zeigen gesucht hat, auch für andere Phänomene von Wichtigkeit zu sein scheint.<sup>3</sup> Auch haben wir einige Bestimmungen ausgeführt, welche über die Frage nach dem Einfluss der Temperatur<sup>4</sup> auf die Wanderungsgeschwindigkeiten orientieren sollten.

Für die Wahl des Silbers als positives Jon sprachen eine Anzahl Gründe; zur Bestimmung des Grenzwertes des molekularen Leitvermögens empfahl sich im Interesse der grösseren Sicherheit ein einwertiges Jon, und Silber ist das einzige einwertige Metall, welches sich — ein grosser Vorteil bei

<sup>1</sup> Hittorf, *Pogg. Annalen*, **89**, 177. **98**, 1. **103**, 1. **106**, 337.

<sup>2</sup> G. Wiedemann, *Pogg. Annalen*, **99**, 177. Kirmis, *Wied. Annalen*, **4**, 503. Weiske, *Pogg. Annalen*, **103**, 466. Kuschel, *Wied. Annalen*, **13**, 289. Lenz, *Mém. de St. Pétersb.* **30**, 1882.

<sup>3</sup> Nernst, *Zeitschr.* **2**, 613 (1888).

<sup>4</sup> Nernst, *Ibid.* 623 (1888).

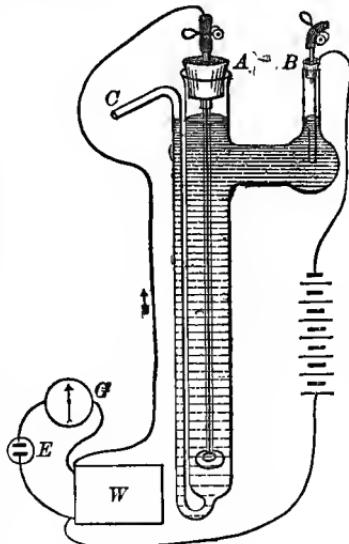
derartigen Messungen — bequem als Elektrode verwenden lässt. Seine Salze sind leicht in genügender Reinheit zu beschaffen. Sodann bot sich uns in der eleganten Titriermethode auf Silber von Herrn Volhard<sup>1</sup> die Möglichkeit, die nötigen Analysen mit grosser Leichtigkeit und durchaus genügender Sicherheit auszuführen.

## 2. APPARAT ZUR BESTIMMUNG DER UEBERFÜHRUNGS-ZAHL

Bei der Wahl desselben suchten wir die Anwendung von Membranen zu umgehen, um störende Nebenwirkungen völlig zu vermeiden, und waren darauf bedacht, seinen innern Widerstand möglichst gering zu machen, damit bei den sehr verdünnten Lösungen, mit denen wir arbeiteten, die Zeitdauer eines Versuchs nicht übermäßig sich ausdehne. Wir sind schliesslich nach mehreren Versuchen bei einem Apparate stehen geblieben, welcher bei seiner Einfachheit sich in vielen Fällen als brauchbar erweisen dürfte. Er besitzt im wesentlichen die Form einer Gay-Lussacschen Bürette und ist in nebenstehender Zeichnung dargestellt. Um das lästige Herabfallen des an der Kathode sich niederschlagenden Silbers zu vermeiden, ist ein seitliches Ansatzrohr — von derselben Weite wie das Hauptrohr — angeschmolzen, welches in einer Kugel endigt, die zur Aufnahme der Kathode dient [951]. Eingeführt wird dieselbe durch das engere Rohr *B*; sie besteht aus einem an einem Silberdraht befestigten und cylindrisch gerollten Silberblech. Die Anode, ein an seinem untern Ende spiralförmig gewickelter Silberdraht, wird durch *A* eingeführt und reicht bis auf den Boden des Gefässes. Um den Eintritt des Stromes in die Lösung nur am unteren Ende zu ermöglichen, ist der gerade Teil des Drahtes mit einer dünnwandigen Glaskapillare überzogen, die sich trotz des

<sup>1</sup> J. Volhard, *Annalen*, 190, 1 (1878). . .

verschiedenen Ausdehnungskoeffizienten von Silber und Glas gut an den Draht anschmelzen liess. Die Oeffnungen *A* und *B* tragen durchbohrte, von kurzen Glasröhrenchen durchsetzte Korke. Das Röhren bei *A* lässt den Elektrodendraht einfach hindurchgehen, während dasjenige bei *B* einen seitlich eingeschmolzenen Platindraht besitzt, an welchem die Elektrode aufgehängt wird. Es kann so *A* durch ein über Draht und Röhren gezogenes Endchen Gummischlauch mittelst Quetschhahn verschlossen, bei *B* mittelst eines Gummischlauchs gesaugt oder geblasen werden, ohne die Elektroden zu erschüttern.



Bei Ausführung eines Versuchs wurde nun ein solcher Apparat samt Elektroden und Korken, aber ohne die Gummierebindungen, gewogen; *A* alsdann in erwähnter Weise geschlossen und bei *B* gesaugt, während die Mündung von *C* unter die Oberfläche der betreffenden Lösung tauchte. Der Apparat füllte sich so bis zur Höhe der oberen Wand des Ansatzrohrs und enthielt, je nach Grösse, 40 oder 60 cc. Lösung. Nunmehr wurde das Ausflussrohr ebenfalls durch ein Gummikäppchen verschlossen, der Apparat aufrecht in einen Wasserthermostaten nach Herrn Ostwald<sup>1</sup> gehängt und, nachdem die Temperatur sich ausgeglichen hatte, die Stromleitung angelegt. Sofort nach Beendigung der Elektrolyse wurde das Ausflussrohr geöffnet und durch Anblasen bei *B* beliebige Teile der Lösung in tarierte Gefässe gefüllt, gewogen und analysiert. Die Menge der im Apparate verbleibenden

<sup>1</sup> Ostwald, *Zeitschr.* **2**, 565 (1888).

Lösung wurde durch die Gewichtszunahme desselben bestimmt. Wenn nun während des Versuchs keine Mischung durch Diffusions- oder Konvektionsströme stattgefunden hat, so wird bei passender Einteilung die zuerst auslaufende Schicht die konzentriertere Lösung an der Anode, sowie genügende Menge unveränderte Lösung enthalten, um vollständig nachzuspülen. Die folgenden Schichten müssen eine unveränderte Konzentration zeigen, während der im Apparat zurückbleibende Anteil die verdünnte Lösung um die Kathode enthält. Die Probe dafür, dass der Versuch brauchbar war, lag also sowohl in dem Unverändertsein der mittleren Schichten, wie darin, dass die Lösung um die Kathode ebensoviel [952] Silber verloren hatte, als diejenige um die Anode mehr enthielt. Nachdem wir die erste Bedingung stets erfüllt gefunden hatten, verzichteten wir schliesslich im Interesse der schnelleren Ausführung der Versuche auf die Entnahme der mittleren Schichten und begnügten uns, die Lösung in zwei etwa gleiche Portionen zu teilen. Wenn, wie es häufig vorkam, ein Wachsen des niedergeschlagenen Silbers von der Kugel aus das Ansatzrohr entlang stattfand, so wurde der Versuch unterbrochen, ehe das Hauptrohr erreicht war.

Die Analysen wurden, wie oben erwähnt, mittels Titration durch Rhodanammoniumlösung ausgeführt, deren Gehalt (etwa  $\frac{1}{100}$  normal) durch oftmaligen Vergleich mit einer Silbernitratlösung ermittelt wurde. Der Titer der letzteren wurde im Laufe der Untersuchungen mehrmals gewichtsanalytisch bestimmt und stets unverändert gefunden. Die Titrationen können eine Genauigkeit bis auf gut  $\frac{1}{50}$  cc. [= 0.038 mg Ag] beanspruchen, besonders da zur Kontrolle der Farbenumschlag stets doppelt beobachtet wurde; es wurde nämlich nach Eintreten der ersten Färbung noch aus einer Pipette 1 cc.  $\frac{1}{100}$   $\text{AgNO}_3$  Lösung zugefügt und wiederum der Farbenumschlag beobachtet.

In die Ueberführungszahl geht ausser der Menge des überführten noch die des gleichzeitig ausgeschiedenen Silbers ein, zu deren Bestimmung man sich bekanntlich am einfachsten eines in den Stromkreis eingeschalteten Silbervoltameters bedient. Da dieselbe aber häufig bei der Untersuchung verdünnter Lösungen weniger als 20 mg betrug, eine so geringe Quantität bei dem schwer völlig zu vermeidenden Verlust kleiner Silberflitterchen sich nicht mit einer genügenden Genauigkeit bestimmen lässt, so haben wir die Elektrizitätsmenge, welche während der Elektrolyse den Apparat durchfloss, durch galvanometrische Messung ermittelt. In den Stromkreis (s. Fig.) wurde ein Stöpselrheostat eingeschaltet, an dessen Enden sich ein Nebenkreis anschloss, welcher ein Galvanometer mit direkter Ablesung und ein Clark-Element enthielt. Durch richtige Wahl des aus dem Rheostaten eingeschalteten Widerstandes  $W$ , sowie passende Schaltung des Elements, kann bekanntlich stets das Galvanometer stromlos gemacht werden; dann ist die

$$\text{Intensität im Hauptkreis } i = \frac{E}{W}, \text{ wo } E \text{ die elektromotorische}$$

Kraft des Normalelementes bedeutet. Da während der Dauer der Elektrolyse, gewöhnlich 4 bis 5 Stunden, die Stromintensität sich wenig und zwar ausserordentlich stetig sich änderte, so genügte es, eine derartige Strommessung, welche sich in wenigen Sekunden ausführen liess, alle zehn Minuten vorzunehmen, um das Stromintegral mit weitaus genügender Sicherheit in der bekannten Weise zu berechnen.

[953] Durch besondere Versuche ergab sich, dass, wenn Widerstandskasten und Element eine Temperatur von 18° besassen, die ausgeschiedene Silbermenge  $f$  sich aus der Formel

$$f = 96.29 \frac{z}{w}$$

berechnen lässt; hier bedeutet  $z$  die Zeitdauer der Elektrolyse in Minuten, und  $w$  den berechneten Widerstand, der, wenn während dieser Zeit die gleiche Elektrizitätsmenge in konstantem Strome den Apparat durchflossen hätte, eingeschaltet werden müsste, um das Galvanometer stromlos zu machen. Betrug die Temperatur von Element und Kasten  $t$ , so war obige Zahl mit  $1 - 0.0012(t - 18)$  zu multiplizieren, wobei sich der Temperaturkoeffizient 0.0012 aus dem des Elements,  $-0.0008$ , und dem des Kastens,  $+0.0004$ , zusammensetzt.

Aus der Thatsache, dass nach Herrn Kohlrausch<sup>1</sup> ein Amper per Sekunde 1.118 mg Ag zersetzt, und der Angabe, dass die Einheit unseres Kastens das legale Ohm war, ergiebt sich (die absolute Widerstandseinheit = 1.063 SE gesetzt) die elektromotorische Kraft unseres Clark-Elementes bei  $18^\circ$  zu 1.431 Volt. Die Zahl stimmt gut mit den Angaben der Herren Lord Rayleigh (1.434 bei  $15^\circ$ ) und v. Ettingshausen<sup>2</sup> (1.433 bei  $13.5^\circ$ ). Auf  $18^\circ$  umgerechnet, geben letztere Werte 1.431 und 1.428, und beweist die Uebereinstimmung unserer Zahl mit diesen, dass wir in der That im Clark-Element einen Etalon für eine elektromotorische Kraft besitzen, bei dessen Anwendung man Fehler über 2 pro mille kaum wird begehen können.

Als Stromquelle dienten uns 38 Leclanché-Elemente, deren elektromotorische Kraft zusammen etwa 40 Volt betrug und welche einen innern Widerstand von etwa 120 Ohm besassen. Um das Auswachsen des Salmiaks zu vermeiden, waren die oberen Ränder der Batteriegläser und der Kohlenstäbe mit Paraffin überstrichen. In einen Widerstand von 5 bis 10000 Ohm geschlossen, liefert die Batterie Stunden lang einen durchaus konstanten Strom und bietet dieselbe ausserdem den Vorteil, stets zum Gebrauch bereit zu sein.

<sup>1</sup> F. Kohlrausch, *Leitf. d. prakt. Physik*, 327 (1887).

<sup>2</sup> Wiedemann, *Elektrizität*, 4, 985 (1885). ,

### 3. DARSTELLUNG DER LÖSUNGEN<sup>1</sup>

Die Lösung von Silbernitrat ( $\text{AgNO}_3$ ) wurde durch Auflösung des krystallisierten Salzes erhalten. Die Silbersalze der Chlorsäure ( $\text{AgClO}_3$ ), [954] Ueberchlorsäure ( $\text{AgClO}_4$ ), Aethylschwefelsäure ( $\text{AgO}_4\text{SC}_2\text{H}_5$ ), Naphthalinsulfonsäure ( $\text{AgO}_3\text{SC}_{10}\text{H}_7$ ), Benzolsulfonsäure ( $\text{AgO}_3\text{SC}_6\text{H}_5$ ), Pseudokumolsulfonsäure ( $\text{AgO}_3\text{SC}_9\text{H}_{11}$ ), Essigsäure ( $\text{AgO}_2\text{C}_2\text{H}_3$ ) wurden durch Abstumpfung der freien Säuren mit feuchtem Silberoxyd und nachheriges Filtrieren durch Asbest dargestellt. Dithionsaures Silber ( $\text{Ag}_2\text{S}_2\text{O}_6$ ) wurde durch Wechselzersetzung äquivalenter Mengen Baryumdithionat und Silbersulfat gewonnen. Um Kieselfluorsilber ( $\text{Ag}_2\text{SiF}_6$ ) zu erhalten, wurde in eine Lösung von Fluorkieselsäure so viel Silberoxyd eingetragen, als dieselbe aufnehmen wollte; darauf wurde so lange Baryumhydratlösung zugetropft, bis sich zu dem niederfallenden Baryumfluorsilikat etwas braunes Silberoxyd gesellte. Die neutrale Lösung wurde filtriert und auf die gewünschte Verdünnung gebracht.

### 4. AUSFÜHRLICHE MITTEILUNG EINES VERSUCHS ALS BEISPIEL

Derselbe wurde bei einer Temperatur von  $26^\circ$  mit etwa  $\frac{1}{100}$  normaler Silbernitratlösung ausgeführt, welche nach Beendigung der Elektrolyse in vier Schichten geteilt wurde. In der folgenden Tabelle befindet sich unter I die Gewichtsmenge der Schichten, unter II die darin gefundene Menge Silber, unter III die Silbermenge, welche darin ohne Elektrolyse enthalten gewesen wäre und sich aus der Angabe berechnet, dass 1 g Lösung 1.139 mg Ag enthielt.

<sup>1</sup> Dieselbe ist von M. Loeb ausgeführt.

TABEL. 1.

Nr.	I	II	III	Diff.
1	20.09 g	39.66 mg	22.88 mg	+16.78
2	5.27	5.96	6.00	-0.04
3	5.33	6.04	6.07	-0.03
4	27.12	14.14	30.89	-16.75
	57.81	65.80		

Wie man sieht, ist der Gehalt der beiden mittleren Schichten 2 und 3 innerhalb der Analysenfehler unverändert geblieben; auch das zweite Kriterium für die Brauchbarkeit des Versuchs, dass nämlich der aus dem Versuche berechnete von dem direkt gefundenen Gehalt nicht differiert, sehen wir sehr nahe erfüllt, indem aus  $\frac{65.80}{57.81} = 1.138$  ein demobigen direkt bestimmten 1.139 nahe kommender Wert sich ergiebt.

Aus der Strommessung in der angegebenen Weise berechnete sich die der durch den Apparat geflossenen Elektricitätsmenge äquivalente Silbermenge zu 32.10 mg, während in einem zur Kontrolle gleichzeitig eingeschalteten [955] Silbervoltameter 32.2 mg sich vorfanden; der erstere Wert, als der zuverlässigere, wurde angenommen.

Die Ueberführungszahl ist aus obigen Daten nach Hittorf<sup>1</sup> folgendermassen zu berechnen. In die Lösung um die Anode (1) sind 32.1 mg Ag ein, aus der um die Kathode (4) ebensoviel ausgetreten. Vor der Elektrolyse führten  $(1 - 0.001139v)$  g Wasser 1.139 mg Ag, wo  $v$  das Verhältnis des Molekulargewichts des Silbernitrats zu dem Atomgewicht des Silbers,  $\frac{170}{108} = 1.57$ , bedeutet. Nach der Elektrolyse waren an der Anode  $(20.09 - 0.03966v)$  g Wasser mit 39.66 mg Ag, an der Kathode  $(27.12 - 0.01414v)$  g Wasser mit 14.14 mg Ag ver-

<sup>1</sup> *Pogg. Annalen*, 98, 19 (1856).

bunden. Die Lösung um die Anode ist somit um  $39.66 - \frac{(20.09 - 0.03966 v)}{1 - 0.001139 v} \cdot 1.139 = (39.66 - 20.09) \times 1.139 (1 + 0.001139 v)$  mg Ag reicher, diejenige um die Kathode um  $\frac{(27.12 - 0.01414 v)}{1 - 0.001139 v} \cdot 1.139 - 16.82 = (27.12 \times 1.139 - 16.82) (1 + 0.001139 v)$  mg Ag ärmer geworden, indem das kleine Defizit der mittleren Schichten zu dem Mindergehalt von Nr. 4 hinzugefügt ist. Wie man sieht, geben die in Tabelle 1 angeführten Differenzen, welche den ersten Faktoren der beiden obigen Produkte entsprechen, nicht genau die Menge der Zu- resp. Abnahme von Ag an, sondern sind mit einem Korrektionsglied behaftet, welches jedoch für Lösungen so geringer Konzentration sehr klein ist. Die Ueberführungszahl, bezogen auf das Anion  $\text{NO}_3^-$ , folgt also zu

$$\frac{16.78}{32.10} \cdot 1.0017, \text{ resp. } \frac{16.82}{32.10} \cdot 1.0017, \text{ im Mittel } 0.524.$$

Nachdem wir wiederholt ein ähnlich günstiges Resultat betreffs des Unverändertseins der mittleren Schichten gefunden hatten, wurde, wie schon erwähnt, schliesslich die Lösung aus dem Apparate meistens in nur zwei Portionen geteilt untersucht.

Da bei dem eben mitgeteilten Versuch in den Stromkreis gleichzeitig noch ein zweiter Apparat eingeschaltet war, so betrug die mittlere Stromintensität nur etwa 0.0012 Amper, die Versuchsdauer 7 Stunden. Im Interesse des schnelleren Arbeitens und um die Batterie mehr auszunutzen, zogen wir es in den meisten Fällen vor, zwei Apparate neben einander zu schalten, wo dann natürlich jeder der beiden Hauptkreise behufs Strommessung einen eigenen Rheostaten enthielt; durch eine geeignete Schaltung wurde dann der Nebenkreis bald an den einen, bald an den anderen [956] Widerstandskasten angelegt, und so in jedem Kreise der Strom gemessen;

bei der so erzielten doppelten Intensität sank die Versuchsdauer auf 3 bis 4 Stunden. Es sei noch erwähnt, dass wir, um ganz sicher zu gehen, das benutzte Clark-Element häufig mit einem zweiten verglichen; die absolute Gleichheit der elektromotorischen Kräfte beider lehrte, dass sich das benutzte Element nicht während der Versuche änderte.

### 5. MESSUNGEN DER UEBERFÜHRUNGSAZHL

Im folgenden bedeutet  $t$  die Versuchstemperatur;  $m$  den Molekulargehalt der Lösung (Grammäquivalente pro Liter);  $f_1$  die aus der Strommessung berechnete Silbermenge in Milligrammen, welche sich im Apparat während des Versuchs ausschied;  $f_2$  dieselbe Grösse, wie sie sich im Silbergalvanometer, welches oft gleichzeitig eingeschaltet, vorfand;  $n$  die Ueberführungszahl, bezogen auf das Anion. Dem Werte von  $n$  ist stets derjenige für  $f_1$  zu Grunde gelegt.

#### *Salpetersaures Silber*

- 1)  $t = 20^\circ$ .  $m = 0 \cdot 1043$ .  $f_1 = 83 \cdot 5$ .  $f_2 = 83 \cdot 6$ .  $n = 0 \cdot 528$ .
- 2)  $t = 26^\circ$ .  $m = 0 \cdot 0521$ .  $f_1 = 76 \cdot 7$ .  $n = 0 \cdot 524$ .
- 3)  $t = 26^\circ$ .  $m = 0 \cdot 025$ .  $f_1 = 48 \cdot 0$ .  $n = 0 \cdot 5223$ .
- 4)  $t = 0^\circ$ .  $m = 0 \cdot 025$ .  $f_1 = 48 \cdot 0$ .  $n = 0 \cdot 5383$ .
- 5)  $t = 26^\circ$ .  $m = 0 \cdot 0105$ .  $f_1 = 32 \cdot 10$ .  $f_2 = 32 \cdot 2$ .  $n = 0 \cdot 524$ .
- 6)  $t = 26^\circ$ .  $m = 0 \cdot 0105$ .  $f_1 = 32 \cdot 10$ .  $f_2 = 32 \cdot 2$ .  $n = 0 \cdot 521$ .

Bei 3) und 4), sowie bei 5) und 6) waren die Apparate in denselben Stromkreis gleichzeitig eingeschaltet.

#### *Chlorsaures Silber*

- 1)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0245$ .  $f_1 = 39 \cdot 88$ .  $f_2 = 39 \cdot 5$ .  $n = 0 \cdot 503$ .
- 2)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0245$ .  $f_1 = 51 \cdot 72$ .  $n = 0 \cdot 499$ .

#### *Ueberchlorsaures Silber*

- 1)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0247$ .  $f_1 = 39 \cdot 88$ .  $f_2 = 39 \cdot 5$ .  $n = 0 \cdot 515$ .
- 2)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0247$ .  $f_1 = 51 \cdot 72$ .  $n = 0 \cdot 512$ .

Bei der Untersuchung dieser beiden Lösungen befand sich 1) mit 1) und 2) mit 2) je im gleichen Stromkreis.

#### *Aethylschwefelsaures Silber*

- 1)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0243$ .  $f_1 = 53 \cdot 80$ .  $n = 0 \cdot 385$ .
- 2)  $t = 24 \cdot 8^\circ$ .  $m = 0 \cdot 0243$ .  $f_1 = 48 \cdot 47$ .  $f_2 = 48 \cdot 34$ .  $n = 0 \cdot 389$ .
- 3)  $t = 25 \cdot 0^\circ$ .  $m = 0 \cdot 00606$ .  $f_1 = 18 \cdot 10$ .  $n = 0 \cdot 384$ .

*Naphthalinsulfonsaures Silber*

- 1)  $t = 29\cdot2^\circ$ .  $m = 0\cdot01292$ .  $f_1 = 33\cdot95$ .  $n = 0\cdot890$ .  
 2)  $t = 25\cdot0^\circ$ .  $m = 0\cdot0250$ .  $f_1 = 39\cdot75$ .  $f_2 = 39\cdot5$ .  $n = 0\cdot886$ .

[957]

*Benzolsulfonsaures Silber*

- 1)  $t = 24\cdot8^\circ$ .  $m = 0\cdot0250$ .  $f_1 = 48\cdot47$ .  $f_2 = 48\cdot84$ .  $n = 0\cdot843$ .  
 2)  $t = 24\cdot7^\circ$ .  $m = 0\cdot0250$ .  $f_1 = 17\cdot85$ .  $n = 0\cdot351$ .

*Pseudokumulsulfonsaures Silber*

- 1)  $t = 24\cdot2^\circ$ .  $m = 0\cdot0238$ .  $f_1 = 61\cdot62$ .  $n = 0\cdot293$ .  
 2)  $t = 29\cdot2^\circ$ .  $m = 0\cdot02216$ .  $f_1 = 38\cdot24$ .  $n = 0\cdot2947$ .  
 3)  $t = 0^\circ$ .  $m = 0\cdot02216$ .  $f_1 = 38\cdot24$ .  $n = 0\cdot2732$ .  
 4)  $t = 0^\circ$ .  $m = 0\cdot02216$ .  $f_1 = 42\cdot79$ .  $n = 0\cdot2731$ .

Bei 2) und 3) befanden sich die Apparate im gleichen Stromkreis.

*Essigsaures Silber*

Bei der Untersuchung dieses Salzes zeigten sich Schwierigkeiten, indem nach Schluss des Versuches die mittelste Schicht nicht unverändert blieb, und der aus dem Versuch sich ergebende Titer der Lösung nicht gut mit dem direkt gefundenen übereinstimmte. Es ist nicht unwahrscheinlich, dass diese Unregelmässigkeiten mit der geringen Löslichkeit des Salzes zusammenhängen, indem sich leicht an der Anode die Lösung so konzentrieren kann, dass festes Salz ausfällt und sich im Laufe des Versuchs zersetzt. Schliesslich gelang es, mit sehr verdünnter Lösung anscheinend brauchbare Resultate zu erhalten.

- 1)  $t = 25^\circ$ .  $m = 0\cdot00972$ .  $f_1 = 20\cdot80$ .  $n = 0\cdot375$ .  
 2)  $t = 24^\circ$ .  $m = 0\cdot00972$ .  $f_1 = 23\cdot99$ .  $n = 0\cdot377$ .

Von Salzen zweibasischer Säuren wurden untersucht: —

*Dithionsaures Silber*

- 1)  $t = 24\cdot8^\circ$ .  $m = 0\cdot0246$ .  $f_1 = 33\cdot40$ .  $n = 0\cdot604$ .  
 2)  $t = 29\cdot2^\circ$ .  $m = 0\cdot0246$ .  $f_1 = 46\cdot70$ .  $n = 0\cdot604$ .  
 3)  $t = 0^\circ$ .  $m = 0\cdot0246$ .  $f_1 = 46\cdot70$ .  $n = 0\cdot605$ .  
 4)  $t = 24\cdot2^\circ$ .  $m = 0\cdot0246$ .  $f_1 = 48\cdot85$ .  $n = 0\cdot606$ .  
 5)  $t = 0^\circ$ .  $m = 0\cdot0246$ .  $f_1 = 45\cdot80$ .  $n = 0\cdot603$ .

Bei 2) und 3) waren die Apparate im gleichen Stromkreis hintereinander geschaltet.

*Kieselfluorsilber*

- 1)  $t = 22.2^\circ$ .  $m = 0.02815$ .  $f_1 = 60.28$ .  $n = 0.467$ .  
 2)  $t = 22.2^\circ$ .  $m = 0.02815$ .  $f_1 = 37.44$ .  $n = 0.464$ .

In Tabelle 2 sind die gewonnenen Resultate der Ueberführungszahlen  $n$  nebst den dazugehörigen Temperaturen und Konzentrationen zusammengestellt:

[958]

TAB. 2.

	<i>n</i>	<i>t</i>	<i>m</i>
Salpetersaures Silber	0.523 0.539	25° 0°	0.1—0.01
Chlorsaures	0.505	25°	0.0245
Ueberchlorsaures	0.514	25°	0.0247
Aethylschwefelsaures	0.385	25°	0.0243—0.0061
Naphthalinsulfonsaures	0.390 0.386	30° 25°	0.0250—0.013
Pseudokumolsulfonsaures	0.293 0.273	25° 0°	0.023
Benzolsulfonsaures	0.347	25°	0.025
Essigsauers	0.376	25°	0.0097
Dithionsaures	0.604 0.604	25° 0°	0.0246
Kieselfluorwasserstoffsaures	0.466	22°	0.0282

Salpetersaures Silber ist eingehend bereits von Herrn Hittorf<sup>1</sup> untersucht worden, welcher etwa vom Gehalte 0.3 abwärts bis 0.024 die Ueberführungszahl ungeändert, im Mittel 0.526 bei 19° fand. Wir finden das gleiche Ergebnis bei Variation des Titers von 0.1—0.01 und einen dem Hittorfschen sehr nahen Wert, nämlich 0.527 auf die gleiche Temperatur umgerechnet. Auch obiger Wert für Silberacetat stimmt gut mit dem Hittorfschen (0.373 bei  $t=15^\circ$  und  $m=0.05$ ).

6. LEITVERMÖGEN DER SILBERSALZE<sup>2</sup>

Dasselbe wurde bei 25° nach der Kohlrauschschen Methode mittelst Telephon und Messbrücke bestimmt. Die Lösungen vom Gehalte  $m=0.025—0.01$  wurden in einem vom Wasserbade eines Thermostaten umgebenen Widerstandsgefäß

<sup>1</sup> *Pogg. Annalen*, **89**, 199 (1853).

<sup>2</sup> Diese Messungen sind von W. Nernst ausgeführt.

nach Herrn Arrhenius<sup>1</sup> untersucht und durch wiederholtes Verdünnen auf die Hälfte, wie von Herrn Ostwald beschrieben, bis auf etwa 0.0008 gebracht. Die unten mitgeteilten Zahlen beziehen sich auf das Leitungsvermögen von Quecksilber=1, indem die von Herrn Kohlrausch bei 18° für Silbernitrat beobachteten Leitvermögen<sup>2</sup> der Berechnung zu Grunde liegen. Zur grösseren Sicherheit der Umrechnung wurde zwischen 18° und 25° der Temperaturkoeffizient bei den Gehalten  $m=0.1$ , 0.02, 0.005 bestimmt und zu 0.0213, 0.0217, 0.0222 gefunden. Der Wert von Herrn Kohlrausch,<sup>3</sup> 0.0221 bei  $m=0.01$ , schliesst sich gut an. In der folgenden Tabelle befinden sich [959] die mittelst dieser resp. interpolierter Temperaturkoeffizienten auf 25° nach den Zahlen von Herrn Kohlrausch<sup>4</sup> umgerechneten und die von uns bei dieser Temperatur durch fortgesetztes Verdünnen gefundenen Werte für das Leitungsvermögen von Silbernitrat.

TAB. 3

$m$	$\lambda \times 10^8$		$m$	$\lambda \times 10^8$	
	K.	L. u. N.		K.	L. u. N.
0.1	1018	1022	0.007	1178	1188
0.05	1071	1086	0.003	1211	1206
0.025	1128	1126	0.0015	1226	1221
0.015	1158	1153	0.0008	1234	1232

Der Parallelismus zwischen beiden Zahlenreihen ist befriedigend. Für die übrigen Salze fanden wir folgende Werte, wobei der Molekulargehalt  $m$  (g-Aequivalente pro Liter) durch Bestimmung der (von eins wenig verschiedenen) spezifischen Gewichte bei 18° aus der analytischen Bestimmung des Gehaltes in Gewichtsprozenten auf diese Tempera-

<sup>1</sup> *Zeitschr.* 2, 563 (1888).

<sup>2</sup> Unter "Leitvermögen" schlechthin sei hier "molekulares Leitungsvermögen" verstanden.

<sup>3</sup> *Wied. Annalen*, 26, 223 (1885).

<sup>4</sup> *Ibid.* 195 (1885).

tur umgerechnet ist. Die Korrektion wegen des Leitungsvermögens des zum Verdünnen benutzten Wassers, welches  $2.5 \times 10^{-10}$  betrug, ist in bekannter Weise angebracht worden. Die wegen Kontraktion der Lösungen beim Verdünnen anzubringenden Korrekturen sind verschwindend.

TAB. 4

<i>m</i>	$\lambda \times 10^8$				
	AgClO <sub>3</sub>	AgClO <sub>4</sub>	AgO <sub>4</sub> SC <sub>2</sub> H <sub>5</sub>	AgO <sub>3</sub> SC <sub>10</sub> H <sub>7</sub>	AgO <sub>3</sub> SC <sub>6</sub> H <sub>5</sub>
0·025	1045	1109	—	—	—
0·015	1103	1139	—	882	846
0·007	1123	1160	905	893	874
0·003	1151	1182	930	926	897
0·0015	1160	1194	943	941	900
0·0008	1163	1200	949	951	906

TAB. 4 (FORTSETZUNG)

<i>m</i>	$\lambda \times 10^8$			
	AgO <sub>3</sub> SC <sub>9</sub> H <sub>11</sub>	AgO <sub>2</sub> C <sub>2</sub> H <sub>3</sub>	$\frac{1}{2}$ Ag <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	$\frac{1}{2}$ Ag <sub>2</sub> SiFl <sub>6</sub>
0·025	734	—	1253	995
0·015	762	—	1343	1020
0·007	791	897	1383	1054
0·003	813	926	1442	1081
0·0015	826	944	1474	1096
0·0008	836	949	1505	1100

[960] Die von Herrn Ostwald<sup>1</sup> an zahlreichen einbasischen Natriumsalzen beobachtete Regelmässigkeit eines sehr nahe gleichen Aktivitätskoeffizienten lässt sich auch leicht an dem hier vorliegenden Material wiederfinden; die Quotienten des Leitungsvermögens eines Salzes bei verschiedenem Gehalte variieren bei den Silberverbindungen einbasischer Säuren nur innerhalb der Grenzen, welche die Beobachtungsfehler kaum überschreiten. Von dieser Thatsache soll Gebrauch gemacht werden, um den Grenzwert des Leitungsvermögens

<sup>1</sup> Ostwald, *Zeitschr.* **2**, 847 (1888).

bei sehr grosser Verdünnung zu erhalten, weil bei der geringsten von uns untersuchten Konzentration 0.0008 die vollständige Dissoziation zwar sehr nahe, aber doch noch nicht völlig erreicht ist. Beachten wir nämlich, dass Silbernitrat nach den Messungen von Herrn Kohlrausch beim Gehalte  $m=0.0008$  im Verhältnis  $\frac{1069}{1077}$  in seine Jonen dissoziiert ist, so werden wir mit ziemlicher Genauigkeit die Grenzwerte von  $\lambda$  auch bei den übrigen einbasischen Silbersalzen erhalten, wenn wir die von uns bei  $m=0.0008$  gefundenen Werte um 0.75% erhöhen.

In Tabelle 5 sind die Messungen verzeichnet, welche wir über den Einfluss der Temperatur auf das Leitvermögen ausgeführt haben; hier wurden an Stelle der platinirten Platinplatten solche aus Silber als Elektroden im Widerstandsgefäß angewendet, wodurch ein sehr deutliches Tonminimum im Telephon erzielt wurde.  $\lambda_0$ ,  $\lambda_{18}$ ,  $\lambda_{28}$  bedeuten die (direkt gemessenen) Leitvermögen bei den Temperaturen  $0^\circ$ ,  $18^\circ$  und  $28^\circ$ ; zieht man, von  $\frac{\lambda_{28}}{\lambda_{18}}$ , 1 ab und dividiert durch 10, so erhält man die Temperaturkoeffizienten zwischen  $18^\circ$  und  $28^\circ$ , welche mit den von Herrn Kohlrausch<sup>1</sup> mitgeteilten direkt vergleichbar sind. Ausserdem ist noch  $\frac{\lambda_0}{\lambda_{25}}$  durch Interpolation berechnet.

TAB. 5

	$m$	$\frac{\lambda_0}{\lambda_{18}}$	$\frac{\lambda_{28}}{\lambda_{18}}$	$\frac{\lambda_0}{\lambda_{25}}$			$m$	$\frac{\lambda_0}{\lambda_{18}}$	$\frac{\lambda_{28}}{\lambda_{18}}$	$\frac{\lambda_0}{\lambda_{25}}$
$\text{AgNO}_3$	0·1	0·638	1·213	0·555	$\text{AgO}_3\text{SC}_6\text{H}_5$		0·005	0·607	1·241	0·519
	0·02	0·638	1·217	0·554	$\text{AgO}_2\text{C}_2\text{H}_3$		0·005	0·611	1·237	0·524
	0·005	0·632	1·222	0·548	$\text{AgO}_3\text{SC}_9\text{H}_{11}$		0·025	0·609	1·242	0·521
$\text{AgClO}_3$	0·005	0·626	1·222	0·542			0·006	0·606	1·246	0·517
	0·005	0·632	1·224	0·547	$\frac{1}{2}\text{Ag}_2\text{S}_2\text{O}_6$		0·025	0·631	1·222	0·547
$\text{AgO}_3\text{SC}_{10}\text{H}_7$	0·005	0·615	1·242	0·526			0·006	0·631	1·226	0·544

<sup>1</sup> Kohlrausch, *Wied. Annalen*, 26, 223 (1885).

### 7. PRÜFUNG DER THEORETISCHEN BEZIEHUNG ZWISCHEN LEITVERMÖGEN UND UEBERFÜHRUNGSAZHL

Hierzu bedarf man ausser der Kenntnis des Grenzwertes des Leitungsvermögens bei unendlicher Verdünnung, welche wir uns soeben zu [961] verschaffen gesucht haben, noch der Ueberführungszahlen für ebenfalls sehr geringe Konzentrationen.

Nun hat, wie schon erwähnt, Herr Hittorf bei  $\text{AgNO}_3$  unter  $m=0\cdot3 n$  von dem Gehalte unabhängig, und wir haben auch an anderen einbasischen Silbersalzen dies Resultat bestätigt gefunden, so dass die von uns bei  $m=0\cdot025-0\cdot01$  gefundenen Zahlen mit dem gesuchten Grenzwert identisch sein dürften. Dieses Resultat leuchtet ohne weiteres ein, wenn man, wie wir es auf Grund unserer Anschauungen annehmen müssen, eine Wanderung der inaktiven Moleküle für ausgeschlossen hält, und bedenkt, dass bei einer Verdünnung von  $0\cdot01$  auf 5550 Molekülen  $\text{H}_2\text{O}$  erst ein Silberion kommt. Dann wird sicherlich die Reibung, welche das Jon bei seiner Fortbewegung erfährt, von der im reinen Wasser nicht verschieden sein. Dass dies selbst bei einer Konzentration von  $m = 0\cdot3$  beim Silbernitrat noch der Fall ist, kann leicht daher röhren, dass bei zunehmendem Salzgehalt die Reibung der beiden Jonen in gleicher Weise (vermutlich verlangsamt) beeinflusst wird.

Die Prüfung des Gesetzes von Herrn Kohlrausch für den Fall sehr grosser Verdünnung lässt sich am einfachsten in der Weise bewerkstelligen, dass man die Grenzwerte des Leitvermögens mit  $(1-n)$ , der Ueberführungszahl des Kations, multipliziert; das Produkt, die molekulare Beweglichkeit des Silberions, muss konstant sein.

TAB. 6

	$\lambda \times 10^8$	$(1-n)$	$\lambda \cdot (1-n) \cdot 10^8$		$\lambda \times 10^8$	$(1-n)$	$\lambda \cdot (1-n) \cdot 10^8$
AgNO <sub>3</sub>	1242	0·477	592	AgO <sub>3</sub> SC <sub>10</sub> H <sub>7</sub>	958	0·614	588
AgClO <sub>3</sub>	1172	0·499	585	AgO <sub>3</sub> SC <sub>6</sub> H <sub>5</sub>	913	0·658	596
AgClO <sub>4</sub>	1208	0·486	587	AgO <sub>3</sub> SC <sub>9</sub> H <sub>11</sub>	842	0·707	595
AgO <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	956	0·615	588	AgO <sub>2</sub> C <sub>2</sub> H <sub>3</sub>	956	0·624	597

Die Beweglichkeit des Ag ergiebt sich aus den verschiedenen Salzen nahezu gleich; die Schwankungen um den Mittelwert,  $591 \times 10^{-8}$ , bleiben innerhalb der Grenzen, welche durch ungünstige Häufung der Beobachtungsfehler gegeben sind. Hierdurch erhalten die neuen Anschauungen über die Elektrolyse eine wiederholte Bestätigung.

Durch obigen Mittelwert, welcher für  $25^\circ$  gültig ist, dürfte die Beweglichkeit des Silberions, falls der den Messungen von Herrn Kohlrausch entnommene Wert für den Grenzwert des Leitvermögens von Silbernitrat keinen in Betracht kommenden Fehler enthält, bis auf wenige Tausendstel sicher gestellt sein. Indem wir aus den bei  $0^\circ$  am salpetersauren und pseudokumulsulfonsauren Silber ausgeführten Bestimmungen [962] von  $n$  (Tab. 2) und dem mittelst  $\frac{\lambda_0}{\lambda_{25}}$  aus Tab. 4 auf  $0^\circ$  umgerechneten  $\lambda$  das entsprechende Produkt bilden,

$$1242 \times 0.461 \times 0.548 = 314 \quad \text{Mittel } 315.5,$$

$$842 \times 0.727 \times 0.517 = 317$$

finden wir die Beweglichkeit des Silberions bei  $0^\circ$  und können so durch Subtraktion dieser Zahl von den auf  $0^\circ$  umgerechneten Leitvermögen der übrigen untersuchten Salze auch zu den Geschwindigkeiten der übrigen Jonen bei  $0^\circ$  gelangen. Uebrigens liegt in der Uebereinstimmung der beiden obigen Werte ein neuer Beweis für die Richtigkeit des zu prüfenden Gesetzes.

In der folgenden Tabelle sind unter I die Jonengeschwindigkeiten bei  $25^\circ$ , unter II diese Grössen bei  $0^\circ$ , unter III die Temperaturkoeffizienten  $\alpha$  zwischen  $25^\circ$  und  $0^\circ$  nach der Formel  $v = v_{25} (1 + \alpha(t - 25))$  berechnet.

TAB. 7

$O_3SC_9H_{11}$	$O_3SC_6H_5$	$O_2C_2H_3$	$O_4SC_2H_5$	$O_3SC_{10}H_7$	$ClO_3$	$Ag$	$ClO_4$	$NO_3$	
I 248	318	361	368	369	587	591	621	640	$\times 10^{-8}$
II 118	156	188	—	180	322	316	347	364	"
III 210	203	197	—	198	181	186	177	175	$\times 10^{-4}$

Wie nahe die unter I aufgeföhrten Beweglichkeiten sich den beobachteten Zahlen anschliessen, lehrt Tab. 8.

TAB. 8

	$\lambda$ beob.	$\lambda$ ber.	Diff.	$n$ beob.	$n$ ber.	Diff.
$AgO_3SC_9H_{11}$	842	889	- 47	0.298	0.295	+ 0.02
$AgO_3SC_6H_5$	913	909	- 4	0.347	0.350	+ 0.03
$AgO_2C_2H_3$	956	952	- 4	0.376	0.379	+ 0.03
$AgO_4SC_2H_5$	956	959	+ 3	0.385	0.384	- 0.01
$AgO_3SC_{10}H_7$	958	960	+ 2	0.386	0.384	- 0.02
$AgClO_3$	1172	1178	+ 6	0.501	0.499	- 0.02
$AgClO_4$	1208	1212	+ 4	0.514	0.512	- 0.02
$AgNO_3$	1242	1240	- 2	0.523	0.524	+ 0.01

Ein Blick auf Tabelle 7, in welcher die Beweglichkeiten nach ihrer Grösse geordnet sind, lässt eine auffallende Beziehung des Temperaturkoeffizienten hierzu erkennen. Mit zunehmender Beweglichkeit nimmt der Temperaturkoeffizient ab. Es sei noch hinzugefügt, dass die entsprechenden Temperaturkoeffizienten der einwertigen Jonen OH und H,<sup>1</sup> welche durch besonders grosse Beweglichkeit ausgezeichnet sind, sich an obige Reihenfolge ebenfalls anschliessen.

<sup>1</sup> Nernst, Zeitschr. 2, 626.

[963]

	OH	H	
I	187	350	$\times 10^{-8}$
III	159	137	$\times 10^{-4}$

Eine Folge dieser Gesetzmässigkeit wäre, dass mit steigender Temperatur die Ueberführungszahlen dem Werte 0·5 zustreben, die Leitvermögen  $\lambda_\infty$  der verschiedenen Salze sich einander nähern.<sup>1</sup>

Suchen wir auch aus den beiden untersuchten Salzen zweibasischer Säuren die Beweglichkeit des Silbers zu berechnen, indem wir aus Tabelle 4,  $\lambda_\infty$  extrapolieren, so ergeben sich

$$\text{aus } \text{Ag}_2\text{S}_2\text{O}_6: 1540 \times 0.394 = 0.607,$$

$$\text{“ Ag}_2\text{SiF}_6: 1120 \times 0.534 = 0.598,$$

somit etwas grössere Zahlen, als bei den einwertigen Salzen. Um nicht mit unseren Anschauungen, wonach dem Silberion, gleichviel ob es durch Dissoziation aus einem ein- oder mehrbasischen Salze entstanden ist, dieselbe Beweglichkeit zuzuschreiben ist, in Widerspruch zu geraten, müssen wir annehmen, dass die von uns bei dem Gehalte 0.025 resp. 0.028 gemessene Ueberführungszahl sich noch mit abnehmender Konzentration ändern muss. Leider war es in dieser Arbeit, welche infolge der Abreise von Einem von uns zum Abschluss gebracht werden musste, nicht möglich, diese Forderung der Theorie zu prüfen; doch sei noch kurz darauf hingewiesen, dass nach der Dissociationshypothese eine Aenderung von  $n$  mit dem Gehalte bei so grossen Verdünnungen, bei denen die binären Elektrolyte bereits eine konstante Ueberführungszahl aufweisen, für die Verbindungen zweibasischer Säuren wahrscheinlich ist. Die Dissociationsprodukte von  $\text{Ag}_2\text{S}_2\text{O}_6$  z. B. sind  $\text{Ag}$ ,  $\text{AgS}_2\text{O}_6$  und  $\text{S}_2\text{O}_6$ ; es geht

<sup>1</sup> Vergl. auch Arrhenius, *loc. cit.* 45 (1884).

daraus hervor, dass selbst bei obigen Verdünnungen neben den Jonen  $+Ag$ ,  $+Ag$ ,  $-S_2O_6$ , auf welche wir soeben Kohlrauschs Gesetz anzuwenden gesucht haben, noch solche in nicht unbeträchtlicher Zahl von der Beschaffenheit  $+Ag$ ,  $-AgS_2O_6$  existieren; mit einer fortschreitenden Dissoziation dieser in jene ist dann natürlich eine Änderung der Ueberführungszahl verknüpft. Es sind hier somit ähnliche Erwägungen anzustellen wie die, durch welche Herr Hittorf bereits vor 29 Jahren<sup>1</sup> gelegentlich der Beobachtung anomaler Ueberführungszahlen bei Jodkadmium die Schwierigkeiten, welche hierdurch seiner Theorie erwuchsen, so glücklich beseitigt hat.

<sup>1</sup> Hittorf, *Pogg. Annalen*, **106**, 546 (1859).

[106] THE RATES OF TRANSFERENCE AND  
THE CONDUCTING POWER OF CERTAIN  
SILVER SALTS<sup>1</sup>

1. INTRODUCTION

WHENEVER a current of electricity is passed through a conductor of the second class, under such conditions that the composition of the solution is not changed, as when a current passes between electrodes of the same metal in a solution of a salt of that metal, curious changes of concentration appear. This was noticed by many scientists, but it was reserved for Hittorf to investigate these changes quantitatively and to advance a plausible and exhaustive hypothesis of their causes. His work constitutes one of the classics in physics; but as it is not, perhaps, so generally known to chemists, a short explanation of his hypothesis may be a not inappropriate introduction to our paper. Taking the example already cited, it is, of course, a familiar principle, that in a given interval the same amount of metal is dissolved from the positive electrode as is deposited upon the negative electrode. If we were to assume that the ions of the electrolyte were incapable of moving independently of each other, the changes in concentration at the two electrodes could only be counterbalanced by the slow process of diffusion, and we should find a deficit in the liquid around the negative electrode corresponding to the amount of metal deposited upon the latter, while all the metal yielded up by the positive electrode would be found

<sup>1</sup> In collaboration with Walther Nernst. Reprinted from *American Chemical Journal*, 11, 106 (1889). This paper is an abbreviated translation of the foregoing monograph, made by Dr. Loeb. [EDITOR].

in its immediate surroundings. This is, of course, an untenable assumption. Supposing, on the other hand, that only the negative ions were immovable, while the positive ones could travel across the liquid as fast as required to supply the places of those disappearing upon the negative electrode: the liquid would be homogeneous at all moments, and there would be no concentration nor dilution around the electrodes. We cannot, however, assume that the negative ions are immovable, everything showing that they move toward the cathode just as well as the positive ones do toward the anode. If both move [107] with equal rapidity, as was tacitly assumed before Hittorf, a little reflection will show that the liquid about the cathode will lose just half as much metal as is deposited upon the electrode, while half the metal given up by the anode to the surrounding liquid will have been transferred toward the cathode. Hittorf's laborious analyses proved that none of these three possibilities was fulfilled. The relation between the changes in concentration and the amount of metal transferred from one electrode to the other proved conclusively that the two classes of ions did not move with equal rapidity; and he showed how this ratio provided a measurement of the share of each class in the total movement. For any salt, [the reciprocal of] the ratio of the weight of the metal deposited to the amount of metal lost by the fluid around the cathode (or its equivalent, the amount gained by that around the anode) represents the share of the negative ion, the anion, in the total movement.

Hittorf has had few followers in these investigations,<sup>1</sup> as the difficulties of experiment were discouraging. Analytical accuracy demanded the use of concentrated solutions, or of

<sup>1</sup> The following list includes all the literature; Hittorf, *Pogg. Annalen*, **89**, 177, **98**, 1, **103**, 1, **106**, 337; G. Wiedemann, *Ibid.* **99**, 177; Weiske, *Ibid.* **103**, 466; Kuschel, *Wied. Annalen*, **13**, 289; Kirmis, *Ibid.* **48**, 503; Lenz, *Mém. Ac. St. Petersbourg*, **30**, 1882.

bulky and cumbrous apparatus, while it was especially desirable to study dilute solutions, and to use apparatus which was not subject to such disturbances as variations of temperature, osmose, and the jars unavoidable during mechanical handling produce. Considerations which will be explained later led us to attempt the acquisition of fresh material, especially with reference to highly dilute solutions. We found that we could do this by studying certain silver salts, mainly organic; and we were led to this choice firstly because silver is the only monovalent metal which furnishes a satisfactory electrode — a matter of some moment for our subsequent work; secondly, because its salts are readily obtained in the needful state of purity; finally, because Volhard's beautiful method of titration<sup>1</sup> enabled us to perform the necessary analyses with great ease and extreme nicety. We also availed ourselves of the opportunity for studying the effects of temperature and concentration upon the velocity of the ions of these salts, because one of us<sup>2</sup> has recently shown how important a part is played by these factors in the kinetics of solutions.

[108] 2. APPARATUS FOR THE DETERMINATION OF THE  
RATE OF TRANSFERENCE

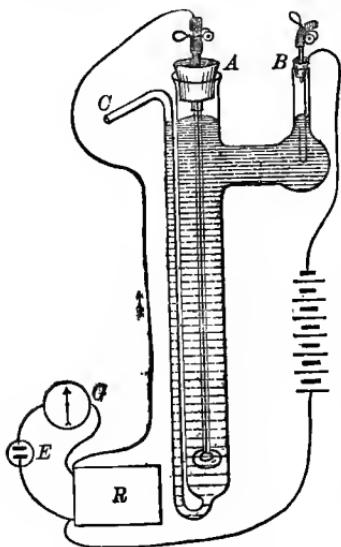
In this apparatus we wished to avoid the use of membranous diaphragms, and to minimize the internal resistance, necessarily large by reason of our very dilute solutions, so as to keep the necessary duration of an experiment within reasonable limits. After various failures we finally hit upon a form whose simplicity is likely to recommend it in similar cases. As shown in the accompanying drawing, it is seen to resemble the Gay-Lussac burette, but with the addition of a short side-tube of the same bore as the main tube. This side-

<sup>1</sup> Volhard, *Annalen*, 190, 1.

<sup>2</sup> Nernst, *Zeitschr. 2*, 613.

tube ends in a bulb, and upon this is set a narrower vertical tube, through which the negative electrode — a cylindrical roll of silver foil fastened to a silver wire — can be let down into the bulb. This works as a sort of pocket, by which masses of the spongy precipitated silver that may become detached from the electrode are prevented from stirring up the body of the solution.

The anode consists of a silver wire rolled into a spiral at the lower end. It is introduced through *A*, and reaches to the bottom of the main tube. In order that the current may enter the liquid only at the spiral, the straight part of



the wire is covered with a capillary of very thin glass, which can be closed around the wire by fusion, in spite of the difference in their coefficients of expansion. The openings *A* and *B* are closed with corks that are traversed by short glass tubes. Of these, the tube at *A* allows free passage to the wire of the electrode. The wall of the tube at *B* is pierced by a platinum wire, which serves to suspend the cathode and to connect it with the conductor of the battery. Thus *A* can be closed by the compression of a bit of rubber tubing drawn over the wire and glass tube, or air can be sucked or blown through a rubber tube connected with *B*, without disturbing the electrodes.

[109] In experimenting, such an apparatus would first be weighed with its electrodes and stoppers, but without the rubber tubing. The latter was hereupon put in position, *A* was closed with a pinch-cock as just indicated, and air was

drawn out at *B* while the nozzle *C* was dipping under the surface of the solution to be used. By this process, the main- and side-tubes were filled up to the level of the top of the latter; the sizes of apparatus we employed contained 40 and 60 cc. respectively. The nozzle was now likewise closed with a rubber cap, and the whole apparatus suspended in one of Professor Ostwald's thermostatic water-baths,<sup>1</sup> in such a fashion that the nozzle protruded over the rim, while the liquid was entirely within the water-bath. After it had acquired the temperature of the bath, the circuit was closed. As soon as the electrolysis was concluded, the nozzle was opened and suitable portions of the liquid were filled into tared vessels, by blowing steadily through *B*. These portions were weighed and analyzed. The portion remaining in the apparatus was estimated by the latter's gain in weight, and likewise analyzed. Provided there has been no mixing through diffusion and convection during the electrolysis, the first portion taken from the apparatus, if the liquid is properly divided, will consist of the stratum around the anode, which has become more concentrated, and of a sufficient quantity of the unaltered middle layers to insure a rinsing of the adhering parts of the lowest stratum. The succeeding portions, being composed wholly of the middle layers, must show an unaltered composition, while what is left in the apparatus includes the diluter strata about the cathode. To prove the reliability of our experiment, we must find in the first place that the middle layers had remained unchanged, and secondly, that the gain of the lowest layer exactly counterbalanced the loss of the highest, for the mean composition of the whole liquid undergoes no change. After finding that the first condition was invariably fulfilled, we saved time by giving up the separate examination of the middle layers, and divided the whole

<sup>1</sup> As described recently by Professor Ostwald, *Zeitschr.* **2**, 565.

liquid into two nearly equal portions. It frequently happened that, during the electrolysis, the electrolyzed silver would grow out from the bulb along the wall of the horizontal tube. In such cases the circuit was broken before the silver had reached the main tube; otherwise, [110] we disconnected whenever we estimated that a sufficient change of concentration had taken place to give the most reliable results.

The analyses were performed, as already intimated, by titration with a solution of ammonic sulphocyanate, the standard of which (about  $\frac{1}{100}$  normal) was ascertained by frequent comparison with an argentic nitrate solution of known strength, occasional gravimetric determinations of which gave absolutely constant results. We claim for the titrations an error well within  $\frac{1}{50}$  cc. (= 0.038 milligrams Ag), each end-reaction being observed twice, as 1 cc. of a  $\frac{1}{100}$  normal solution of argentic nitrate was added from a pipette, after the first appearance of the characteristic tint, and the titration repeated.

The ratio we are seeking to determine requires, besides the data of the change in concentration, the weight of the silver which has been actually deposited upon the cathode, in the same interval of time. This would most naturally be determined by a silver voltameter placed in the same circuit with the apparatus. But as the examination of dilute solutions often necessitated the deposit of less than 20 milligrams in all, and the silver is deposited in such a form upon the voltameter that it is difficult to weigh it without a slight loss, we found it to be more advantageous to determine the quantity of electricity which traversed the apparatus by galvanometric measurement. A resistance-box was introduced into the circuit for this purpose (see figure), to the extremities of which a second circuit was connected, containing a Clark's cell and

a galvanometer with direct reading. The Clark's cell being introduced in the proper direction, it is well known that a suitable resistance  $R$  may be introduced by means of the box, which will put the galvanometer at rest at the  $O$  point; when this is effected, we have for the electrical intensity of the main

current  $i = \frac{E}{R}$ ,  $E$  denoting the electromotive force of the standard Clark's cell.

As the intensity of the current changed but little and very gradually during the four or five hours which were usually occupied by an electrolysis, we were satisfied with making this measurement, which required but a few seconds' attention, every ten minutes. The total amount of electricity could then be integrated with sufficient certainty.

Special experiments showed that, when resistance-box and [111] Clark's cell were at a temperature of  $18^{\circ}$  C., the quantity  $f$  of precipitated silver could be found by the formula,

$$f = \frac{\tau}{r} 92.69,$$

where  $\tau$  represents the duration of the electrolysis in minutes, while  $r$  denotes the resistance which would have been necessary to keep the galvanometer at  $O$ , provided that amount of electricity which actually passed through the apparatus had done so in a current which remained constant throughout this interval. Whenever the resistance-box and the cell were at any other temperature,  $t$ , the above expression must be multiplied with the factor  $1 - 0.0012(t - 18)$ . This coefficient of temperature, 0.0012, is derived from that of the cell, -0.0008, and that of the box, +0.0004.

Our battery consisted of 38 Leclanché cells, with a combined electromotive force of about 40 volts and an internal resistance of about 120 ohms. It furnished a current which

remained practically constant for many hours, when enclosed in a circuit of 5000–10,000 ohms resistance. It also had the advantage of being always ready for use.

### 3. PREPARATION OF THE SILVER SOLUTIONS

The solutions of argentic nitrate were prepared from the crystallized salt. Those of the chlorate, perchlorate, ethyl-sulphonate, naphthalene-sulphonate, benzene-sulphonate, pseudo-cumene-sulphonate and acetate, were made by neutralizing known amounts of these acids with moist argentic oxide, passing the solution through an asbestos filter, and diluting to a suitable volume. Argentic dithionate ( $\text{Ag}_2\text{S}_2\text{O}_6$ ) was obtained by the reaction of exactly equivalent quantities of baric dithionate and argentic sulphate. To make argentic fluosilicate, a solution of hydrofluosilicic acid was saturated with argentic oxide; dilute baric hydrate solution was then added cautiously, until the brown color of argentic oxide commenced to appear in the precipitate of baric fluosilicate. The neutral solution was then filtered and diluted.

### 4. DESCRIPTION OF A DETERMINATION IN DETAIL

The description of this determination, made with a solution of argentic nitrate which was about  $\frac{1}{10}$  normal, will best illustrate our method of experiment and calculation. The electrolysis was [112] conducted at a temperature of  $26^\circ$ , and the solution thereupon divided into four portions, which are numbered in the following table in the order in which they were taken out; consequently, No. 1 represents the *lowest* stratum in the apparatus. Column I contains the weights of these portions; II, the amount of silver found in each; III, the amount each portion would have contained if no change had occurred, estimated from the fact that 1 gram of the solution originally contained 1.139 milligram of silver.

TABLE I

Portion	I	II	III	Diff.
1	20.09 grams	39.66 millig.	22.88 millig.	+16.78 millig.
2	5.27	5.96	6.00	- 0.04
3	5.83	6.04	6.07	- 0.03
4	27.12	14.14	30.89	- 16.75
	57.81	65.80		

It will be seen that the strength of two middle portions has remained constant, within the errors of determination; we also find a close agreement in the second test, which demands that the mean concentration shall remain unchanged; the value  $65.80/57.81 = 1.138$ , scarcely different from the original strength 1.139.

The measurement of the electrical current as described above informed us that a quantity of electricity equivalent to the precipitation of 32.10 mg. of silver had passed through the apparatus; while a silver-voltameter, placed in the circuit for our better assurance, contained 32.2 mg.; the former value was accepted as the more trustworthy.

Following Hittorf,<sup>1</sup> we based these calculations upon our data: The solution at the anode (1) received from the latter 32.1 mg. Ag, and the uppermost layer (4) gave up the same amount to the cathode. Owing to the changes in concentration, the values in the above table are not absolutely correct, since 1 gram of solution does not always contain the same weight of water, as had been provisionally assumed. But the necessary correction is small and readily made. Let  $\nu$  be the ratio of the molecular weights of silver and the salt in question; in this special case  $\nu = \frac{170}{108} = 1.57$ . Let  $a$  represent the amount of silver contained in 1 gram of [113] unaltered solution, being consequently dissolved in  $(1 - a\nu)$  grams of water. If, after electrolysis,  $q$  grams of the solution about one electrode are found to contain  $b$  grams of silver, the

<sup>1</sup> Hittorf, *Pogg. Annalen*, 98, 19.

gain or loss will be represented by  $\pm b - \frac{a(q-b\nu)}{1-a\nu} = \pm \frac{b-aq}{1-a\nu}$ .

As  $b-aq$  is the value given in the column of differences, the factor  $\frac{1}{1-a\nu}$  represents the necessary correction. Consequently, after completing the deficit of portion 4 by the addition of the small deficits in 2 and 3, we have for the *rate of transference of the negative ion*,

$$\frac{16.78}{32.10} 1.0017 \text{ and } \frac{16.82}{32.10} 1.0017, \text{ or a mean value of } 0.524.$$

As already stated, the determination was usually simplified by dividing the liquid into two portions instead of four.

In this experiment there was a second apparatus placed in series in the circuit; hence the mean intensity of the current was only 0.0012 ampère, and the electrolysis lasted seven hours. We frequently saved time and used our battery to better advantage by performing two simultaneous electrolyses in parallel circuits, each of which must, of course, contain its own resistance-box; by means of a properly constructed switch, we could apply the measuring circuit to either box at will, thus securing the measurement of both electrolyses with the same galvanometer and element. We may also state here that the last was frequently compared with another cell of the same construction and was always found to be exactly equivalent to it in electro-motive force, a proof that it did not vary during the course of our experiments.

### 5. RATES OF TRANSFERENCE OF THE NEGATIVE ION

Hereafter  $t$  implies the temperature during electrolysis;  $m$  the molecular concentration (gram-molecules per liter);  $f_1$  the milligrams of silver precipitated on the cathode accord-

ing to galvanometric measurement;  $f_1$  the same value according to the voltameter whenever it was used;  $n$  the rate of transference.

*Argentic Nitrate*

1) $t = 20^\circ$	$m = 0 \cdot 1043$	$f_1 = 83 \cdot 5$	$f_2 = 83 \cdot 6$	$n = 0 \cdot 528$
2) $t = 26^\circ$	$m = 0 \cdot 0521$	$f_1 = 76 \cdot 7$		$n = 0 \cdot 524$
3) $t = 26^\circ$	$m = 0 \cdot 0250$	$f_1 = 48 \cdot 0$		$n = 0 \cdot 5223$
4) $t = 0^\circ$	$m = 0 \cdot 0250$	$f_1 = 48 \cdot 0$		$n = 0 \cdot 5383$
5) $t = 26^\circ$	$m = 0 \cdot 0105$	$f_1 = 32 \cdot 10$	$f_2 = 32 \cdot 2$	$n = 0 \cdot 524$
6) $t = 26^\circ$	$m = 0 \cdot 0105$	$f_1 = 32 \cdot 10$	$f_2 = 32 \cdot 2$	$n = 0 \cdot 524$

[114] In 3) and 4) and in 5) and 6) both pieces of apparatus were in the same circuit.

*Argentic Chlorate*

1) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0245$	$f_1 = 39 \cdot 88$	$f_2 = 39 \cdot 5$	$n = 0 \cdot 503$
2) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0245$	$f_1 = 51 \cdot 72$		$n = 0 \cdot 499$

*Argentic Perchlorate*

1) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0247$	$f_1 = 39 \cdot 88$	$f_2 = 39 \cdot 5$	$n = 0 \cdot 515$
2) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0247$	$f_1 = 51 \cdot 72$		$n = 0 \cdot 512$

In studying these two solutions, 1) and 1) and 2) and 2) were in the same circuits.

*Argentic Ethyl-sulphonate*

1) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0243$	$f_1 = 58 \cdot 30$		$n = 0 \cdot 385$
2) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0243$	$f_1 = 48 \cdot 47$	$f_2 = 48 \cdot 34$	$n = 0 \cdot 389$
3) $t = 25^\circ$	$m = 0 \cdot 00606$	$f_1 = 18 \cdot 10$		$n = 0 \cdot 384$

*Argentic Benzene-sulphonate*

1) $t = 24 \cdot 8^\circ$	$m = 0 \cdot 0250$	$f_1 = 48 \cdot 47$	$f_2 = 48 \cdot 34$	$n = 0 \cdot 343$
2) $t = 24 \cdot 7^\circ$	$m = 0 \cdot 0250$	$f_1 = 17 \cdot 85$		$n = 0 \cdot 351$

2) of the former and 1) of the latter solution were electrolyzed in series.

*Argentic Pseudocumene-sulphonate*

1) $t = 24 \cdot 2^\circ$	$m = 0 \cdot 0235$	$f_1 = 61 \cdot 62$		$n = 0 \cdot 293$
2) $t = 29 \cdot 2^\circ$	$m = 0 \cdot 02216$	$f_1 = 38 \cdot 24$		$n = 0 \cdot 2947$
3) $t = 0^\circ$	$m = 0 \cdot 02216$	$f_1 = 38 \cdot 24$		$n = 0 \cdot 2732$
4) $t = 0^\circ$	$m = 0 \cdot 02216$	$f_1 = 42 \cdot 79$		$n = 0 \cdot 2731$

2) and 3) were electrolyzed in series.

*Argentic Naphthalene-sulphonate*

1) $t = 29 \cdot 2^\circ$	$m = 0 \cdot 01292$	$f_1 = 33 \cdot 95$		$n = 0 \cdot 390$
2) $t = 25 \cdot 0^\circ$	$m = 0 \cdot 0250$	$f_1 = 39 \cdot 75$	$f_2 = 39 \cdot 5$	$n = 0 \cdot 386$

*Argentic Acetate*

In examining this salt, we were surprised to find that the middle layers of the solution did not remain unchanged, and that the mean concentration after electrolysis did not agree with the [115] original standard. This irregularity is probably due to the slight solubility of the salt, since it can easily happen that the solution about the anode becoming over-concentrated, some of the salt crystallizes out and vitiates the result. In fact, we did succeed in obtaining reliable values when we had recourse to a highly dilute solution.

1) $t = 25^\circ$	$m = 0.00972$	$f_1 = 20.80$	$n = 0.375$
2) $t = 24^\circ$	$m = 0.00972$	$f_1 = 23.99$	$n = 0.377$

*Argentic Dithionate*

1) $t = 24.8^\circ$	$m = 0.0246$	$f_1 = 33.40$	$n = 0.604$
2) $t = 29.2^\circ$	$m = 0.0246$	$f_1 = 46.70$	$n = 0.604$
3) $t = 0^\circ$	$m = 0.0246$	$f_1 = 46.70$	$n = 0.605$
4) $t = 24.2^\circ$	$m = 0.0246$	$f_1 = 48.85$	$n = 0.606$
5) $t = 0^\circ$	$m = 0.0246$	$f_1 = 45.80$	$n = 0.608$

2) and 3) were electrolyzed in series.

*Argentic Fluosilicate*

1) $t = 22.2^\circ$	$m = 0.02815$	$f_1 = 60.28$	$n = 0.647$
2) $t = 22.2$	$m = 0.02815$	$f_1 = 37.44$	$n = 0.647$

In Table II we summarize these values of  $n$ , with the corresponding temperatures and concentrations.

TABLE II

Argentic	$n$	$t$	$m$
Nitrate . . . . .	0.523	25°	{ 0.1 - 0.01
	0.539	0°	
Chlorate . . . . .	0.505	25°	0.0245
Perchlorate . . . . .	0.514	25°	0.0247
Ethyl-sulphonate . . . .	0.385	25°	0.0248 - 0.0061
Naphthalene-sulphonate . .	0.390	30°	{ 0.0250 - 0.013
	0.386	25°	
Pseudocumene-sulphonate .	0.293	25°	{ 0.023
	0.273	0°	
Benzene-sulphonate . . . .	0.347	25°	0.025
Acetate . . . . .	0.376	25°	0.097
Dithionate . . . . .	0.604	25°	{ 0.0246
	0.604	0°	
Fluosilicate . . . . .	0.466	22°	0.0282

Argentic nitrate has been carefully studied by Hittorf,<sup>1</sup> who found that between the concentrations 0.3 and 0.024 the rate of transference does not vary, the mean value being 0.526 at 19°. We came to the same conclusions for variations of concentration [116] from 0.1 to 0.01, and we found a value which, when reduced to the same temperature, very nearly agreed with his, 0.527 at 19°. The acetate result given above also agrees well with Hittorf's (0.373 where  $t=15^{\circ}$  and  $m=0.05$ ).

## 6. CONDUCTING POWER OF THE SILVER SALTS AND ITS RELATION TO THE RATE OF TRANSFERENCE

It will be noted that the rate of transference is a value varying with the compound, since it merely expresses the share of the one ion in the total movement. If  $u$  is the actual velocity of the positive ion and  $v$  that of the anion,

$$n = \frac{v}{u+v}; \text{ and the rate of the positive ion, } 1-n = \frac{u}{u+v}.$$

Kohlrausch,<sup>2</sup> as is well known, has propounded the simple hypothesis that the conducting power of a molecule of an electrolyte is represented by the sum of the velocities of its ions,

$$\lambda = u + v.$$

His experiments, however, did not seem to give the requisite support to this theory, some salts giving approximate results, but those of weak bases and acids giving utterly discordant figures. The difficulty is removed if we assume that the conduction is not performed by all the molecules of the electrolyte, but only by those whose ions are actually in independent motion. This is Arrhenius's principle of conductive activity.<sup>3</sup> Kohlrausch's values for molecular conduc-

<sup>1</sup> *Pogg. Annalen*, **89**, 199.

<sup>2</sup> Fr. Kohlrausch, *Wied. Annalen*, **6**, 1.

<sup>3</sup> S. Arrhenius, *Sur la conductibilité*, etc., Stockholm, 1884.

tivity are a function of the total number of molecules of the electrolyte between the electrodes; according to Arrhenius, the coefficient of activity, i.e., the proportion of molecules actually engaged in conduction, not only varies for different compounds, but also increases for any one compound with its dilution, and approaches unity for extreme dilutions. It is only in this limiting case that Kohlrausch's equation becomes absolutely true; this is the view that Kohlrausch himself had expressed with regard to his law, whose accuracy, he said, could only be tested by experiments with highly dilute solutions. Ostwald's examination of the conducting power of highly attenuated solutions of a very large number of electrolytes<sup>1</sup> has afforded very valuable support to these recent views.

Since, however, the quantities  $u$  and  $v$  are so closely connected [117] with the rate of transference of the ions, a study of the latter in dilute solutions must afford powerful means of testing the truth of Kohlrausch's law with Arrhenius's emendations. This was the chief motive of our work, and we must now, therefore, proceed to compare the values which we have given in section 5 with the conducting power of the same salts. Accordingly, the necessary measurements of conduction were made by one of us (W. N.), by Kohlrausch's method which with various valuable modifications has been described by Professor Ostwald.<sup>2</sup> The values which we present are scaled upon the conducting power of mercury as unity, and the calculations are based upon Kohlrausch's determination of the molecular conductivity of argentic nitrate.<sup>3</sup>

The following table gives the conducting power of the dif-

<sup>1</sup> *Zeitschr.* **1**, 61 and 97.

<sup>2</sup> *Ibid.* **2**, 563.

<sup>3</sup> As Kohlrausch worked at 18°, while the present determinations were made at 25°, the coefficients of temperature were determined by special experiments for various dilutions of AgNO<sub>3</sub>. For the details of these results we must refer to the German version of our paper.

ferent silver salts. The molecular concentration (gram-molecules in the liter)  $m$ , was calculated from the percentage composition as found by analysis, and the specific gravity determined at  $18^\circ$ , although this barely differed from that of water. There was no appreciable contraction when additional water was added for dilution; but a proper correction was made for the conduction by the water itself, which was found to be  $2.5 \times 10^{-10}$ .

TABLE III

$m$	$\lambda \times 10^8$ at $25^\circ$				
	$\text{AgNO}_3$	$\text{AgClO}_3$	$\text{AgClO}_4$	$\text{Ag}(\text{C}_2\text{H}_5\text{SO}_4)$	$\text{Ag}(\text{C}_6\text{H}_5\text{SO}_4)$
0.025	1126	1045	1109	...	...
0.015	1153	1103	1139	...	846
0.007	1188	1128	1160	905	874
0.003	1206	1151	1182	930	897
0.0015	1221	1160	1194	948	900
0.0008	1232	1163	1200	949	906
 $m$					
	$\lambda \times 10^8$ at $25^\circ$				
	$\text{Ag}(\text{C}_9\text{H}_{11}\text{SO}_3)$	$\text{Ag}(\text{C}_{10}\text{H}_7\text{SO}_3)$	$\text{AgC}_2\text{H}_5\text{O}_2$	$\frac{1}{2}\text{Ag}_2\text{S}_2\text{O}_6$	$\frac{1}{2}\text{Ag}_2\text{Si F}_6$
0.025	734	...	...	1253	995
0.015	762	882	...	1343	1020
0.007	791	893	897	1383	1054
0.003	813	926	926	1442	1081
0.0015	826	941	944	1474	1096
0.0008	836	951	949	1505	1100

[118] Ostwald has found <sup>1</sup> that the sodium salts of numerous monobasic acids have almost identically progressing coefficients of activity; the same regularity may be observed in the present series. The ratios of the conductivity of a salt in various states of dilution agree, for the silver salts of the monobasic acids, within limits that scarcely transcend the probable errors of observation. We shall utilize this fact in finding the limit of the conductivity for extreme dilution; for, at the concentration 0.0008, the dissociation of the molecules is not yet complete, although very nearly so. If we remember that, according to Kohlrausch's measurements, when

<sup>1</sup> Ostwald, *Zeitschr.* **2**, 847.

$m = 0.0008$ ,  $\frac{1069}{1077}$  of the molecules of argentic nitrate are dissociated, we can fairly assume that the limiting values of  $\lambda$  for the other silver salts may be obtained by raising by 0.75 per cent the values found for  $m=0.0008$ .

Table IV summarizes the measurements made to determine the effect of temperature upon conducting power; in these the platinum electrodes usually employed were replaced by silver ones, which gave very sharp readings. The measured conductivities at  $0^\circ$ ,  $18^\circ$ , and  $28^\circ$  are denoted by  $\lambda_0$ ,  $\lambda_{18}$  and  $\lambda_{28}$  respectively; to obtain the coefficient of temperature

$\frac{\lambda_{28}}{\lambda_{18}}$  must be diminished by 1 and divided by 10;  $\frac{\lambda_0}{\lambda_{25}}$  was

calculated from such an interpolated value of  $\lambda_{25}$ .

TABLE IV

	$m$	$\frac{\lambda_0}{\lambda_{18}}$	$\frac{\lambda_{28}}{\lambda_{18}}$	$\frac{\lambda_0}{\lambda_{25}}$
$\text{AgNO}_3$	0.1	0.638	1.213	0.555
	0.02	0.638	1.217	0.554
	0.005	0.632	1.222	0.548
$\text{AgClO}_3$	0.005	0.626	1.222	0.542
$\text{AgClO}_4$	0.005	0.632	1.224	0.547
$\text{AgC}_6\text{H}_7\text{SO}_3$	0.005	0.615	1.242	0.526
$\text{AgC}_6\text{H}_5\text{SO}_3$	0.005	0.607	1.241	0.519
$\text{AgC}_2\text{H}_5\text{O}_2$	0.005	0.611	1.237	0.524
$\text{AgC}_6\text{H}_{11}\text{SO}_3$	0.025	0.609	1.242	0.521
	0.006	0.606	1.246	0.517
$\frac{1}{2}\text{Ag}_2\text{S}_2\text{O}_8$	0.025	0.631	1.222	0.547
	0.006	0.631	1.226	0.544

[119] 7. TEST OF THE LAW OF KOHLRAUSCH FOR  
EXTREME DILUTIONS

For this purpose we need, besides the limiting values for conduction, which we have just shown to be attainable, the limiting values for the rate of transference, likewise for extreme dilution.

At the close of section 5 we noted that Hittorf found the value of  $n$  to be independent of the state of dilution where

$m < 0.3$  in the case of  $\text{AgNO}_3$ , and that we confirmed his result by our own experiments on this and other salts. Consequently the values found for this rate, whenever  $m = 0.025 - 0.01$ , can be assumed to hold good for infinite dilutions. The reason becomes apparent when, considering the inactive molecules as stationary, we remember that a molecular concentration 0.01 means a proportion of one silver ion to 5550 molecules of  $\text{H}_2\text{O}$ . The resistance which such an ion would encounter cannot differ from that of pure water.

The testing of Kohlrausch's law can now be readily accomplished by multiplying the limiting value of conductivity into  $(1-n)$ , the rate of transference of the positive ion; the product, which represents the molecular velocity of the silver ion, must remain constant for all the monobasic salts.

TABLE V

	$\lambda \times 10^8$	$(1-n)$	$\lambda (1-n) 10^8$
$\text{AgNO}_3$	1242	0.477	592
$\text{AgClO}_3$	1172	0.499	585
$\text{AgClO}_4$	1208	0.486	587
$\text{AgC}_2\text{H}_5\text{SO}_4$	956	0.615	588
$\text{AgC}_{10}\text{H}_7\text{SO}_3$	958	0.614	588
$\text{AgC}_8\text{H}_5\text{SO}_3$	913	0.653	596
$\text{AgC}_9\text{H}_{11}\text{SO}_3$	842	0.707	595
$\text{AgC}_2\text{H}_5\text{O}_2$	956	0.624	597

The velocity of Ag as found in these salts proves to be nearly constant: the deviations from the average  $591 \times 10^8$  are within the limits of the probable errors of observation, especially as the latter have a cumulative effect. We consider this an additional confirmation of the recent electrolytic hypotheses.

This average, which applies for  $25^\circ$ , may be considered the true value for the velocity of the Ag ion, within a few thousandths, provided Kohlrausch's determination of the limit of conduction for argentic nitrate contains no important error.

We can now calculate the ion's velocity at 0°, from the values of  $n$  at that temperature for argentic nitrate and pseudocumol-sulphonate (Table II), and [120] the values of  $\lambda$  reduced from Table III by the ratio  $\frac{\lambda_0}{\lambda_{25}}$  (Table IV).

$$\begin{array}{l} 1242 \times 0.461 \times 0.548 = 314 \\ 842 \times 0.727 \times 0.517 = 317 \quad \text{Mean} = 315.5. \end{array}$$

We again call attention to the smallness of the deviation. Now, since  $\lambda = u + v$ , we can obtain the velocities of all our negative ions, by subtracting the velocity of the silver from the respective conducting powers. In Table VI we find on the first line the velocities at 25°; on the second, those at 0°; on the third, the coefficient of temperature between 25° and 0°, as calculated from the formula  $v = v_{25}[1 + \alpha(t - 25)]$ ,  $\alpha$  being the coefficient: all the values must be multiplied by the factor given in the final column.

TABLE VI

	$C_9H_{11}SO_3$	$C_6H_5SO_3$	$C_2H_5O_2$	$C_2H_5SO_4$	
I.	248	318	361	368	$\times 10^{-8}$
II.	118	156	183	...	$\times 10^{-8}$
III.	210	203	197	...	$\times 10^{-4}$
	$C_{10}H_7SO_3$	$ClO_3$	Ag	$ClO_4$	$NO_3$
I.	369	587	591	621	640
II.	180	322	316	347	364
III.	198	181	186	177	175

The close agreement of the velocities shown in line I with the observations of the rates of transfer and of the conduction, is proved by the fact that the calculated and observed values agree within one half per cent in all cases. A glance at Table VI, in which the velocities are arranged according to magnitude, will bring out a striking relation of the coefficients of temperature. *The coefficient of temperature decreases when the velocity increases.* We may add that the coefficients of temperature for the monovalent ions OH and H, which

have an exceptionally great velocity, can be added to this series.<sup>1</sup>

	OH	H	
I.	187	350	$\times 10^{-7}$
III.	159	137	$\times 10^{-4}$

A result of this regularity would be that, as the temperature rises, the rates of transference would all approach the value 0.5, and the conducting powers  $\lambda_\infty$  of all salts would approach equality.<sup>2</sup>

If we attempt to calculate the velocity of the silver ion from [121] the salts of the two dibasic acids which we have studied, we obtain from

$$\begin{aligned} \text{Ag}_2\text{S}_2\text{O}_6: 1540 \times 0.394 &= 0.607 \\ \text{Ag}_2\text{SiF}_6: 1120 \times 0.534 &= 0.598 \end{aligned}$$

These values are somewhat greater than those found before. To avoid a conflict with the necessary assumption that the free ion of silver must have the same velocity, no matter whether it has been liberated from a mono- or dibasic acid ion, we must admit that the rates of transfer in these two salts, which were measured at a concentration 0.025 and 0.028 respectively, must change on further dilution. As our investigation was brought to a close by the departure of one of us from Leipzig, we were unable to set this question at rest; we note in passing, however, that the dissociation hypothesis makes it probable that the compounds of multivalent radicals are still undergoing changes at dilutions in which mono-basic compounds show a constant rate of transference. The dissociation products for  $\text{Ag}_2\text{S}_2\text{O}_6$ , for instance, are  $\text{Ag}$ ,  $\text{AgS}_2\text{O}_6$  and  $\text{S}_2\text{O}_6$ ; consequently in such dilutions as 0.025 there may exist, besides the ions  $+\text{Ag}$ ,  $-\text{Ag}$ ,  $-\text{S}_2\text{O}_6$ , upon which we based our calculations, a considerable set of ions  $+\text{Ag}$ ,  $-\text{AgS}_2\text{O}_6$ ; if these decompose on further dilution, the

<sup>1</sup> Nernst, *Zeitschr.* **2**, 626.

<sup>2</sup> Compare Arrhenius, *loc. cit.*, p. 45.

rate of transference must continue to change. We have here considerations similar to those which Hittorf used so skillfully nearly thirty years ago,<sup>1</sup> in obviating the difficulties which the abnormal behavior of cadmic iodide threatened to cast in the way of his theory.

<sup>1</sup> Hittorf, *Pogg. Annalen*, **106**, 546 (1859).

[300] THE USE OF THE GOOCH CRUCIBLE AS  
A SILVER VOLTAMETER<sup>1</sup>

FOR the exact measurement of electric currents, no method is more convenient and more free from objections than the determination of the amount of silver deposited from a neutral solution of a silver salt. The sole source of error, especially where weak currents are concerned, arises from the imperfect adhesion of the silver upon the cathode. The latter is generally a platinum crucible, and the silver, except for densities of current not always attainable, is deposited in minute scales and needles, instead of forming a coherent coating. In the subsequent washing and decantations, those particles are readily detached and carried away, and a loss is occasioned which becomes very appreciable when the total deposit does not exceed a few centigrams. A Gooch crucible, with asbestos felting over the holes, would be a far better form of cathode, if it would only hold the solution during electrolysis without leaking. I have attained this very satisfactorily, by replacing the ordinary platinum cap with a glass siphon of the shape indicated in Fig. 1.

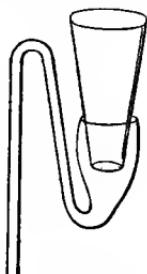


FIG. 1.

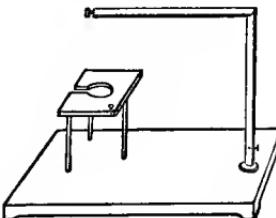


FIG. 2.

<sup>1</sup> Reprinted from *Journal of the American Chemical Society*, 12, 300 (1890).

The crucible is made on a rather taller and narrower pattern than is usual, and it fits quite snugly into the upper portion of the cup [301] of the siphon. The two are united by a bit of rubber drawn over the junction; the rubber should be freed from sulphur, although there is no real danger of contact with the silver solution.

The apparatus is filled with the silver nitrate solution, so that the top of the siphon is not quite reached and is set upon the stand, Fig. 2. After the completion of the electrolysis, adding a little liquid causes the siphon to act and to drain off every drop of nitrate solution, without in any way disturbing the deposit; the lixiviation with hot water is equally expeditious, and the crucible can then be detached from the siphon, dried and weighed.

The stand for this voltameter is seen in Fig. 2. The crucible is hung in a brass block, the conical hole in which fits exactly around its upper third; to this block the negative wire of the circuit is to be attached.

The positive wire is connected with a long horizontal cone, which is isolated from the cast-iron base, and from which the silver cone that forms the anode is suspended within the crucible by a silver wire.

## [145] IS CHEMICAL ACTION AFFECTED BY MAGNETISM? <sup>1</sup>

THE close relationship between electricity and chemical affinity on the one hand, and that between electricity and magnetism on the other, have naturally raised the question whether any relation can be traced between affinity and magnetism.

This question was the subject of numerous investigations during the entire first half of this century,<sup>2</sup> but appears to have dropped out of sight, until Professor Remsen,<sup>3</sup> in 1882, again attracted attention to it by the interesting observation that, from a solution of the sulphate, copper is unequally deposited upon the armature of a horse-shoe magnet. Other experiments by Messrs. Nichols and Franklin,<sup>4</sup> and Messrs. Rowland and Bell,<sup>5</sup> have also borne relation to this question. I have nevertheless ventured to approach the subject from a new side, with the conviction that all of these investigations introduce phenomena which tend to obscure the point of issue, i.e., the effect of magnetism upon the chemical reaction itself. This will be made clear by an analysis of the principles upon which these investigations have been conducted; they can be divided into four categories.

The earliest experiments regarded the rusting of bar magnets; and the most trustworthy observers appear to invalidate the assertion of a few, that magnetized iron differs from

<sup>1</sup> Reprinted from *American Chemical Journal*, **13**, 145 (1891).

<sup>2</sup> For full literature see E. Wartmann, *Philosophical Magazine*, **30**, 266.

<sup>3</sup> *American Chemical Journal*, **3**, 137.

<sup>4</sup> *American Journal of Science*, **34**, 419; **35**, 290.

<sup>5</sup> *Philosophical Magazine*, **34**, 419; **35**, 105.

the non-magnetized [146] metal in this respect, or that the north and south poles show dissimilar behavior. The experiments were naturally crude, and a positive result, were it admitted, would obviously have been due to a polarized arrangement of the molecules, rather than to variations in chemical affinity.

Next came the crystallization of salts or metals from a solution, within and without a magnetic field. Quite a number of observers appear to have found that the *direction* of growth, either of the crystals themselves or of the clusters which they form, can be affected by the presence of a magnetic field, even though the substance be a diamagnetic. But what is there in this that involves a modification of chemical action? The quantity of deposit has not been observed to be altered by the magnet; the physical arrangement of the molecules during crystallization is always governed by directive forces having no connection with affinity, and to the ordinary ones is now superimposed the polarizing influence of the magnet.

A different principle is involved in Remsen's experiments, for they depend upon the removal of particles from a magnetized mass of iron, and the substitution therefor of faintly-magnetic copper. The explanation of Messrs. Rowland and Bell must appear highly plausible, that the resistance to such removal must protect the more highly magnetized points from reaction, so long as there are places where the iron can be more readily dissolved. We have here a purely mechanical reason for the localization of the reaction, in a non-uniform field. That the *total* amount of reaction would not be affected we may infer from a recent experiment by Fossati,<sup>1</sup> in which he shows that the weight of iron precipitated from a solution by zinc is not affected by the presence of a strong magnetic field.

<sup>1</sup> *Bulletino dell' Elettricista*, 1890. I quote from Wiedemann's *Beiblätter*, 1890, p. 1010, which alone is at my disposal.

Apparently inconsistent with the protection-hypothesis are the observations of Messrs. Nichols and Franklin, which show that iron which has become passive through the action of strong nitric acid suddenly regains its activity when introduced into a magnetic field. One might be tempted to ascribe this to the exposure of fresh surfaces, owing to the rearrangement of the molecules during magnetization; but since the investigators have reason to seek the cause in the induction of local electric currents by the magnet, [147] we may assign this phenomenon to the fourth category, that of galvanic action in the magnetic field. To my knowledge, Messrs. Nichols and Franklin were the first to experiment upon the effect of an unequal magnetic field upon an electrolyte: the movement of the paramagnetic salt to the interior portions of the field, and the inequality of electric potential consequent upon the variation of concentration, were proved, as might be expected. We have, then, this effect, as well as that of the Faradic induction, to account for any irregularities which the galvanoscope might indicate, when a solution undergoing electrolysis was also subjected to magnetic influence. Messrs. Nichols and Franklin do ascribe their observations to this cause, and see no reason to introduce a supposed change of the chemical conditions.

I fail to see any significance in the experiment of placing one of two gas-voltameters, or one of two cells containing an iron solution,<sup>1</sup> in a magnetic field, and looking for a difference in the amount of decomposition when a current is passed through the couple in series. Surely no such result could be expected in the face of the universally acknowledged Law of Faraday, unless, indeed, a magnetic field were imagined to alter the quantivalence of the elements.

To sum up: all experiments hitherto made have introduced

<sup>1</sup> Fossati.

non-chemical phenomena, due either to the inequalities of the magnetic field, or to the physical heterogeneity of the reacting system, or to both of these causes at once. It was my wish to study the effect of magnetism upon chemical reaction where the system remained homogeneous throughout, and where the field of stress was practically homogeneous. Such conditions can be realized by observing the speed of some reaction which does not involve solids, in the presence of a magnet, and, again, when there is no magnetic effect, provided the magnetic properties of the system could be altered by the reaction. In the same manner as an electric system is affected by its approach to or removal from a magnetic field, we might suppose that a reaction which made a system more or less amenable to magnetic action might show evidence of acceleration or retardation by the magnetic force. If this effect were appreciable, the relation between magnetic force and affinity would be established, and data could be obtained for calculating the real value of magnetization.

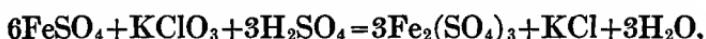
[148] My results, however, have been negative, and I am led to believe that no such relation exists, unless it be so slight that my means of observation have been inadequate. Being confident, however, that my method has been of no lower order of delicacy than those hitherto employed in connection with the subject, I do not hesitate to assert that the interesting effects which have been noted are not due to a variation of affinity or of chemical reaction in its strictest sense. For this reason I herewith present my results:—

The choice of material for my investigation was rather limited: of all compounds, the salts of the iron group alone yield markedly paramagnetic solutions; furthermore, Wiedemann has shown that the ordinary form of reaction between salts does not affect the total magnetism of the system, so long as it involves merely an interchange of acids. But there is a

marked change when the constitution of one of the ingredients is altered: the atomic magnetism of trivalent iron is 25 per cent greater than that of the same element in the ferrous state. I resolved, therefore, to study the effect of magnetism upon the speed of oxidation and reduction of iron salts in solution by reagents which showed but a feeble magnetism by themselves.

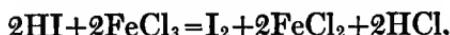
Two such reactions have already been studied under ordinary conditions, and, inasmuch as the methods employed seemed admirably suited to my purpose, I have followed them in this investigation.

Dr. J. J. Hood<sup>1</sup> determined the speed of the reaction



by estimating volumetrically with permanganate the amount of ferrous salt remaining unaffected at different stages of the process.

Meyerhoffer<sup>2</sup> gives one series of observations upon the reaction



in which case the iodine which had been set free could be determined with starch paste and sodic thiosulphate.

#### OXIDATION OF A FERROUS SALT

I had at my disposal a large Ruhmkorff electro-magnet, with cylindrical iron cores ten inches long and three inches thick. [149] With the poles three inches apart, and with a current from ten storage cells, the intensity of the magnetic field was roughly determined at 10,000 c. g. s. per square-centimeter. For my supply of electricity I am indebted to the kindness of the director of the Physical Laboratory, Professor A. A. Michelson. While ten cells were usually employed, I

<sup>1</sup> *Philosophical Magazine*, [5], 6, 371; 8, 121; 13, 419.

<sup>2</sup> *Zeitschr.* 2, 597.

sometimes was enabled to use double that number, and in several instances obtained the current directly from the dynamo, employing as full a current as the apparatus would safely bear. Because the results were always virtually identical, no pains were taken to determine the exact strength of the magnetic field, but 18,000 c. g. s. is a low estimate of the maximum reached.

The axes of the cores being horizontal, a prismatic battery cell,  $2\frac{1}{2} \times 6 \times 6$  inches, was placed between the poles to serve as a bath of constant temperature. It was therefore protected from direct contact with the poles by thin layers of cotton batting, and was traversed by a rapid current of water from a reservoir whose contents were kept within  $0.1^{\circ}$  C. of the desired temperature.

The solutions were contained in a sort of pocket-flask of 100 cc. capacity, an inch thick, and having two flat sides of circular outline three inches in diameter. This flask was suspended in the bath in such a manner as to be just between the poles of the magnet. The solutions which were not to be subjected to the influence of the magnet were contained in a precisely similar flask, and the water-bath in which this was placed was fed by the overflow from the first mentioned one. Where it was not feasible to observe the two reactions at the same time, especial care was taken to keep the temperature constant.

The following solutions were employed: a one-third molecular solution of potassium chlorate, a one-half molecular solution of sulphuric acid, a one-half molecular solution of ferrous sulphate, a solution of potassium permanganate of which 12.5 cc. corresponded to 1 cc. of the iron solution. The latter was made from crystallized ferrous sulphate, with a little sulphuric acid and an excess of metallic iron, so that it was very nearly neutral.

Proper volumes of the chlorate and the acid solutions having been run into the flask and sufficient water to make the volume 80 cc., the solution was allowed to acquire the temperature of the water-bath. Thereupon 20 cc. of the ferrous sulphate solution, which had been brought to the same temperature, were added [150] rapidly, the flask was vigorously shaken, and at once replaced in the water-bath. If the magnet was to be employed, its electric circuit was closed at this time. After the expiration of a few minutes, 10 cc. were withdrawn from the flask by means of a pipette, and were quickly run into a large quantity of cold water contained in a porcelain dish, the time being noted when the pipette was emptied. The titration was then executed as rapidly as possible. This operation was repeated at suitable intervals, until the solution was exhausted or external conditions prevented a continuation of the observation. Where two reactions were to be observed together, the second solution was mixed ten minutes after the first, the same interval being preserved, as nearly as might be, throughout. Owing to the weakness of the permanganate solution and to varying conditions of illumination, my titrations have a probable error of fully  $\frac{1}{20}$  to  $\frac{1}{15}$  cc., but this is in no unfavorable proportion to the observed values; in cases of over-coloration I rejected the result, rather than titrate back with another solution.

The reaction has been proved by Hood to be subject to the law

$$\frac{dx}{dt} = C(A-x)(B-x),$$

where  $x$ =the amount of substance changed,  $t$ =time elapsed,  $A$  and  $B$  represent the original quantities of ferrous sulphate and chlorate respectively, and  $C$  is a coefficient depending on external circumstances.

As equivalent quantities of  $A$  and  $B$  were used,

$$\frac{dx}{dt} = C(A-x)^2.$$

Integrating,  $\frac{1}{A-x} = Ct + \text{constant.}$

Calculating this constant from the initial conditions  $d=0$ ,  $x=0$ , constant  $= \frac{1}{A}$ , and consequently

$$C = \frac{1}{At} \cdot \frac{x}{A-x}.$$

$A$  is the amount of permanganate required at the first titration, and  $A-x$  represents the amount of each subsequent one, after the lapse of  $t$  minutes. We possess all the data for calculating  $C$ . This coefficient has been shown by Hood to depend upon the temperature, to be augmented by the presence of free [151] acid, and diminished by the presence of neutral salts not participating in the reaction. It is consequently decreasing continually during the reaction, most noticeably, however, toward the end. Furthermore, if magnetism is of influence, the values of  $C$  must show it. In order to eliminate the other influences, I have sought to take the samples from corresponding solutions at the same intervals of time, and have varied the conditions somewhat by changing the temperatures as well as the amounts of sulphuric acid present in different series.<sup>1</sup> It will be seen that, while there is considerable variation between individual determinations, these variations are no greater between analogous samples of two corresponding series than between two succeeding samples of the same series. Further, the means of the whole series agree well with each other. The tables which I subjoin are selected, solely with reference to their general reliability, from a larger

<sup>1</sup> In this connection it may be interesting to note that this reaction is, according to my experiments, barely perceptible at 0°C., — a result which agrees closely with the limit set by Dr. Hood by extrapolation with his temperature-coefficient.

mass of material, all of which gave analogous results. While the effect of magnetism should produce acceleration, the variations of *C* from that of the non-magnetic reaction are negative quite as frequently as positive.

Series I.— $\text{KClO}_3 + 6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4$ . Temperature,  $10.2^\circ$ .

Series II.—Same conditions, in magnetic field (10 cells).

<i>t</i>		<i>A—x</i>		<i>C</i>	
I	II	I	II	I	II
0	0	24.98	24.26	...	...
30.25	29.75	22.78	22.88	0.49524	0.48357
105	104.25	20.22	20.28	8050	7940
155.17	154.86	18.71	18.68	8011	7951
210	210	17.49	17.27	7695	7942
241	241.33	16.82	16.79	7546	7599
305.25	305.5	15.64	15.53	7491	7584
Mean		0.48051		0.47895	
Mean of last five		0.47758		0.47803	

Series III.—Same relation,  $\text{KClO}_3:\text{FeSO}_4$ ; great excess  $\text{H}_2\text{SO}_4$ . Temperature,  $18.7^\circ$ .

Series IV.—Same as III, but with magnet (20 cells).

Series V.—Same as III, but with magnet (dynamo).

[152]

<i>t</i>			<i>A—x</i>			<i>C</i>		
III	IV	V	III	IV	V	III	IV	V
0	0	0	23.16	23.10	23.10	...	...	...
20	20	20.5	18.57	18.39	18.32	0.35335	0.35543	0.35509
40	40	40	15.33	15.45	15.41	5513	5558	5400
60	60	60	13.28	13.38	13.21	5353	5241	5401
80	80.5	80	11.71	11.58	11.42	5276	5348	5584
100	100.25	100	10.41	10.45	10.40	5288	5227	5286
120	120	120	9.38	lost	9.45	5282	...	5211
139.75	130.75	140	8.72	8.99	8.54	5116	5197	5272
160.25	155	161	7.94	8.17	7.84	5164	5104	5233
Mean			0.35292			0.35288		
						0.35355		

### REDUCTION OF FERRIC CHLORIDE

The reaction  $2\text{HI} + 2\text{FeCl}_3 = \text{I}_2 + 2\text{FeCl}_2 + 2\text{HCl}$ , is not a simple one, being reversible, and furthermore accompanied by complicating bye-reactions. It seemed better to avoid all

attempts to obtain the reaction-coefficients, and to make parallel experiments, with exactly the same time-intervals. If the magnetic force had any effect, this must be visible from the burette-readings.

The method used was exactly as before, but diluted solutions were employed to prevent the loss of free iodine. Equivalent quantities of hydriodic acid and ferric chloride were allowed to react in  $\frac{1}{100}$  molecular solutions, and 10 cc. were

taken out at a time and titrated with  $\frac{1}{115}$  normal sodium thiosulphate solution. The determinations were very exact, and the corresponding burette-readings will be found to correspond so closely as to leave no doubt of the exact equality of speed within and without the magnetic field. I give all the series which were observed; in the second set, the reaction was carried as far as it would go,—at least there was no more iodine liberated after  $15\frac{3}{4}$  hours' standing.

Temperature,  $17.8^{\circ}$ .

Time	Without Magnet,		With Magnet (dynamo)	
		$\text{Na}_2\text{S}_2\text{O}_3$ required		$\text{Na}_2\text{S}_2\text{O}_3$ required
30·5	3·89		30·5	3·95
60	4·80		60	4·52
120	5·10		120	5·10
180	5·55		180	5·40
231	5·60		231	5·58

[153] Same conditions.

Time	Without Magnet		With Magnet (dynamo)	
		$\text{Na}_2\text{S}_2\text{O}_3$ required		$\text{Na}_2\text{S}_2\text{O}_3$ required
40	5·99		40	5·92
86	6·92		85	6·93
130	7·38		130	7·38
205	7·85		205	7·90
266	8·07		266	8·04
325	8·28		325	...
375	8·32		375	8·30
			1330 <sup>1</sup>	8·28

<sup>1</sup> Without magnet.

Same proportions; temperature, 0°.

Time	Without Magnet		With Magnet (10 cells)	
		$\text{Na}_2\text{S}_2\text{O}_8$ required		$\text{Na}_2\text{S}_2\text{O}_8$ required
60		2·70	60.5	2·80
120		3·72	120	3·70
195		4·54	195	4·42
275		4·86	275	4·90
360		5·20	...	...
380		5·70	380	5·80
480		6·06	480	6·10
600		6·43	600	6·60
705		6·71	705	6·75

[263] APPARATUS FOR THE DELINEATION OF  
CURVED SURFACES, IN ILLUSTRATION OF  
THE PROPERTIES OF GASES, ETC.<sup>1</sup>

IN attempting the graphic representation of the relations between the volume, temperature and pressure of gases, or of other problems involving three variables, one is met by the difficulty of properly constructing the surfaces in question. Drawing isothermals, etc., as projected upon a single plane, gives a very imperfect idea of the actual proportions. For many years this method has been occasionally supplanted by the actual construction, in papier maché or plaster, of models bounded on one side by the surface in question,—relief maps, in other words. This plan suffers from several disadvantages. Aside from the notion of solid volume which is involuntarily entertained in beholding such a model, some of the surfaces are too complex to be well shown in this manner. Furthermore, the models are rather hard to make, expensive, and occupy a good deal of room.

I have obviated most of these difficulties by obtaining a set of glass plates, about 11 cm. square and 7 mm. thick, ruled in squares 7mm. wide. Placed one on top of the other, these form a block whose perpendicular edge may be taken for the third axis in a system of rectangular coördinates. Having drawn upon a sheet of paper the curves representing the relation between volume and pressure as successively  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ , etc., of temperature, I can trace them, with suitable grease-chalks, upon the successive glass plates. When these are

<sup>1</sup> Reprinted from *Journal of the American Chemical Society*, **13**, 263 (1891). Also *Chemical News*, **65**, 220 (1892).

superposed, the curves exhibit the proper relations in space and afford a very fair idea of the nature of the surface of which they are elements, without arousing any sensation of an included volume. Since the lines can always be erased and replaced by others, a set of twenty plates suffices for all purposes, and the surfaces can be produced at a moment's notice if the necessary sketches on paper are preserved. Besides [264] being useful for illustrating lectures in molecular physics, the plates can also be employed to advantage in the construction of crystallographic, geological and other models.

Where the parallax, inevitable for glass plates, becomes annoying, it is possible to substitute wide-meshed cotton netting, stretched upon square frames of uniform thickness. The curves can be embroidered upon the net, as it were, with pieces of colored thread; although it is not quite so easy to make the lines conform to the drawing, the general effect remains the same.

## [1019] NOTE ON THE CRYSTALLIZATION OF SODIUM IODIDE FROM ALCOHOLS<sup>1</sup>

AN accidental observation during the preparation of some ethers by Williamson's method led to the experiments detailed below, which are [1020] merely presented as an addition to the somewhat restricted literature upon the addition products between haloid salts and alcohols.

Sodium iodide is very soluble in absolute methyl alcohol and is not precipitated therefrom upon the addition of a considerable volume of absolute ether, while wet ether produces immediate separation. On cooling a warm solution, rather large plate-shaped crystals separate out, while a solution saturated at room temperature and then cooled below 0° becomes thoroughly permeated with brilliant white felted needles; although differing markedly in appearance, these two kinds of crystals are identical in composition.

The iodine was determined by Volhard's method; the methyl alcohol, by heating in a current of air and absorbing the vapors in sulphuric acid; the gain in the weight of the latter corresponding accurately to the loss experienced by the crystals. The results agreed very closely with the formula  $\text{NaI} \cdot 3\text{CH}_3\text{O}$ , — 38.91 and 38.55 per cent of methyl alcohol and 51.50 per cent of iodine (calculated for  $\text{NaI} \cdot 3\text{CH}_3\text{O}$ , 39.06 and 51.58 per cent).

Potassium iodide, while fairly soluble in alcohol, crystallizes free from it, and this seems to be quite a characteristic distinction between the two salts. Sodium iodide crystallizes from ethyl alcohol, forming an addition product, although not

<sup>1</sup> Reprinted from *Journal of the American Chemical Society*, 27, 1019 (1905).

quite so readily as with the methyl alcohol. The analysis gave 64.22 per cent I; calculated for  $\text{NaI.C}_2\text{H}_6\text{O}$ , 64.91 per cent. This, therefore, seems to be the formula of the addition product with ethyl alcohol.

Normal propyl alcohol dissolves nearly one-third of its weight of sodium iodide and, on evaporation at low temperatures, deposits crystals which appear to have the formula  $5\text{NaI.3C}_3\text{H}_8\text{O}$ , as two distinct preparations gave 68.26 per cent, and 68.22 per cent of iodine, against 68.27 per cent required by theory. Apparently, therefore, the molecular proportion of alcohol assimilated decreases as the series ascends.

## THE VAPOR FRICTION OF ISOMERIC ETHERS<sup>1</sup>

THE recorded experiments on the friction of vapors, by the transpiration method, having been made with cumbersome apparatus and at the temperature corresponding to the boiling points of the substances, it was thought important to devise a method whereby non-saturated vapors could be studied at identical temperatures, for the purpose of ascertaining whether the constitution as well as the composition of organic compounds influences the molecular volume, of which the vapor-friction is a function.

The apparatus used consists of a U-tube, one limb of which, about 60 cm. long, has a bore of less than one tenth of a millimeter, while the bend and the other limb is just wide enough to allow a column of mercury to descend unbroken. A stop-cock and funnel-end are placed on the wider tube, which also bears two marks about 50 cm. apart. The capacity of the tube between these marks is accurately determined. The whole apparatus can be heated uniformly, as it is surrounded by a vapor-jacket. Before heating, the liquid to be studied is poured into the tube and is vaporized as the temperature rises, in such a manner as to expel all air and foreign gases. A short column of mercury, of known length, is introduced by means of the stop-cock, and in its descent forces the vapor through the capillary; the time in which the lower meniscus travels from the upper to the lower mark is ascertained by means of a stop-watch. The method is easy and rapid, and experiments with air gave results agreeing well among themselves and with the values obtained by the majority of previ-

<sup>1</sup> In collaboration with F.S.M. Peterson. Reprinted from *Science*, 21, 818 (1905).

ous observers. The calculations were made according to Poiseulle's formula, very few corrections being necessary.

From the study of isomeric ethers, as well as ethyl alcohol, it was found that the constitution has a decided influence upon the internal friction of the vapor, as will be seen from the following table, representing in each case the average of a number of experiments. The last column gives the comparative volumes of the molecules according to the formula suggested by L. Meyer, in which Y is the friction, M the molecular mass.<sup>1</sup>

$$V = .00003 \left( \frac{M(1+at)}{Y^2} \right) \frac{3}{4}$$

Substance	Y	V
Methyl ether, $(CH_3)_2O$	1133.5	55.53
Ethyl alcohol, $C_2H_6O$	1100	58.09
Methyl-ethyl ether	1030	78.2
Ethyl-ether	944.7	110.4
Methyl-propyl ether	951.8	100.74
Methyl-isopropyl ether	992.3	96.46
Ethyl-propyl ether	874.9	133.2
Di-propyl ether	797.6	170.7
Di-isopropyl ether	841.5	157.8

<sup>1</sup> The editor has been unable to find the original source of this equation, which is doubtless of a highly hypothetical nature.

[652] ANALYSIS OF SOME BOLIVIAN BRONZES<sup>1</sup>

THROUGH the kindness of the authorities of the American Museum of Natural History, we were enabled to analyze portions of certain implements collected in the region around Lake Titicaca. It will be seen that these metals differ remarkably in composition, and indicate the possession of considerable metallurgical skill by the inhabitants of that region. The absence of the slightest traces of silver may be taken as a proof that the tin was derived from cassiterite, rather than native tin. The composition of Specimen IV suggests its preparation from domeykite, or some other copper arsenide, fairly free from sulphur. Owing to the small mass of samples, which were drilled or cut from the specimens, the density determinations, made with water in a pycnometer, are only approximate. In Specimen VI the porosity of the material undoubtedly occasioned a low result. Tin and copper were separated by potassium [653] polysulphide, the former determined as stannic oxide and the latter electrolytically. Arsenic was separated from copper by Crookes's method, and sulphur was weighed as barium sulphate after oxidation with nitric acid in a sealed tube.

I. Museum No. 1842. Small chisel or pinch-bar,  $18 \times 1\frac{1}{8} \times \frac{1}{2}$  inches. Very tough. Density, 8.68.

II. Museum No. B-1840. Implement 5-6 inches long, very hard and tough; pale color. Density, 8.94.

III. Museum No. 1959. Thick wide chisel  $4\frac{1}{2}$  inches long, tough but less hard. Density, 8.92.

<sup>1</sup> In collaboration with S. R. Morey. Reprinted from *Journal of the American Chemical Society*, 32, 652 (1910).

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IV. Museum No. 1-859. Socketed spear-head, 12 inches long. Density, 8.89.

V. Museum No. 2413. Fragment of pointed bar 6 inches long. Density, 8.61.

VI. Museum No. 1949. Small cast chisel; contained characteristic air-holes or "pipes." Apparently contained considerable *oxide*. Density, 8.18 (?).

## ANALYSIS

	I	II	III	IV	V	VI
Cu.....	91.81	90.51	95.59	97.43	94.96	91.43
Sn.....	7.56	8.92	4.48	.....	4.98	7.05
Pb.....	.....	.....	.....	trace(?)	.....	.....
Fe.....	trace	trace	trace	trace	.....	trace
S.....	.....	trace	.....	little	0.53	.....
As.....	.....	.....	.....	2.14	.....	.....
	—	—	—	—	—	—
	99.37	99.43	100.07	99.57	100.47	98.48

To this report may be added the record of an analysis, made in 1901, by Dr. A. E. Hill with one of us, of a figurine found in Honduras. Color, pale yellow; density, 8.94-6. Cu. 93.19, Sn 1.64, Pb 1.60, Fe 0.40 per cent; Au, Sb and Zn absent.

## [601] STUDIES IN THE SPEED OF REDUCTIONS<sup>1</sup>

FOR some years past, I have been conducting experiments to ascertain whether certain phenomena due to the mixture of derivatives of closely allied bases might not indicate the formation of complex bases of a higher order, similar to the well-known complex acids. The difference in the colloidal tendencies of mixed and pure basic salts, the appearance of spectroscopic lines in a mixture of oxides, none of which emit these lines in a pure state, the curious relation of thorium and cerium with respect to incandescence, are among the phenomena which might call for such an explanation. While my experiments have so far failed to yield positive evidence in this direction, I have obtained certain results which seem worth recording for their own sake.

My first attempts concerned themselves with the possible formation of an aluminic-ferric complex, by the hydrolysis of the mixed chlorides. Solutions representing systematic variations in concentration and relative proportion of ferric and aluminic hydroxides were observed for several years and finally analyzed, with the result that I am convinced that no aluminum is carried down permanently combined with basic ferric chlorides. Any temporary occlusion is compensated on standing with the supernatant acid solution of ferric chloride.

But a complexity of these two bases might be indicated, if the behavior of ferric chloride toward reducing agents were affected by aluminic chloride, especially since the latter would hardly be likely to figure as a chlorine-carrier in dilute solutions. When these experiments yielded a positive result,

<sup>1</sup> Reprinted from *Orig. Com. Eighth International Congress of Applied Chemistry*, 26, 601 (1912).

other chlorides were mixed with ferric chloride to test their effect upon its stability toward reducing agents. The method followed closely that employed by A. A. Noyes, in studying the speed of reaction between ferric chloride and stannous chloride. He mixed dilute [602] solutions of these two salts in equivalent proportions, drew measured samples from time to time, running them into a solution of mercuric chloride, to arrest the reaction by removing all the remaining stannous chloride without affecting the trivalent iron; then determining the amount of the latter by titration with potassium dichromate. Using twentieth normal solutions of these two compounds, I obtained constants for the reaction agreeing closely with Noyes's figures; upon adding aluminic chloride, also in twentieth normal concentration, the speed was more than doubled; while it was quadrupled in the presence of a tenth normal solution of aluminic chloride. Of course, such a result might be ascribed to the excess of chlorine ions present, especially as Noyes had found that hydrochloric acid has an effect, though of a different kind. If so, chlorides of divalent elements should not have so great an effect: yet  $1/20$  normal solutions of manganeseous chloride and of glucinic chloride also double the speed of reduction, although the ionization cannot be the same. A  $1/20$  normal solution of quadrivalent thorium does not accelerate quite as much.

As is well known, Noyes considers this as a typical reaction of the third order, and shows that his equation

$$c_3 = \frac{1}{2r} \left( \frac{1}{(A-X)^2} - \frac{1}{A^2} \right)$$

applied to his experimental data, gives a fairly constant value for  $c_3$ . My series, which I cannot reproduce in full, show about the same degree of constancy for  $c_3$ . Consequently, I think it fair to assume that the reaction remains of the same type,

and that the variations in speed are due to the specific influences of the metals concerned. For, as will be seen, the accelerations are not exactly the same. I give average values of  $c_3$ , always for the reaction between 1/20 normal ferric and stannous chlorides.

	$c_3$
Without admixture	67·8
[603] With 1/20 AlCl <sub>3</sub>	149·6
With 1/20 MnCl <sub>2</sub>	161·2
With 1/20 GICl <sub>2</sub>	159·4
With 1/20 ThCl <sub>4</sub>	157·0
With 1/10 AlCl <sub>3</sub>	288·1
With 1/10 MnCl <sub>2</sub>	266·4
With 1/20 SnCl <sub>4</sub>	225·0
With 1/40 SnCl <sub>4</sub>	181·0

The last two values are anomalous; but expectedly so, as this compound enters into the original reaction.

Noyes has found that the addition of free hydrochloric acid alters the nature of the reaction, so that it becomes one of the second order. I find that several chlorides, notably zirconium chloride and oxychloride, have a similar effect. The reason must be different from Noyes's explanation, based on free chlorine ions.

Another series of experiments, with the same fundamental object, sought to study the influence of analogous compounds on ceric sulphate. Cerium, alone of the so-called rare-earth group, lends itself to studies in oxidation and reduction, although virtually no work has been done in following these changes quantitatively. Of the salts of the tetravalent base, only the sulphate is stable in aqueous solution, and then only in the presence of much free acid. On standing, its orange color fades very slowly, a marked odor of ozone indicating the by-product of its reduction to the cerous state. Indeed, I am doubtful whether I have ever had a solution of the tetravalent salt, free from any trivalent admixture. After many trials I found that a fair idea of a reduction speed might

be obtained by mixing cerium sulphates and glucose in equimolecular amounts in dilute solution, maintaining at 25° C., and titrating samples with very dilute hydrogen dioxide solution, which instantaneously completes the decolorization of the ceric salt. The reaction with glucose is completed in about two hours and can be readily followed in 15-minute intervals. Of course, the stability of the hydrogen peroxide standard was meanwhile controlled with permanganate solution.

For some unexplained reason, the reaction as studied by me does not follow a logarithmic law: the amount of cerium reduced is simply proportionate to the elapsed time, so that  $x/t$  is pretty nearly constant for every individual series. So anomalous a [604] behavior naturally precludes any claim on rigid deduction. But the experiments had comparative values, when they were compared with others, in which equivalent quantities of lanthanum sulphate and thorium sulphate had been mixed with the solution of cerium salts.

Values of  $x/10t$

Pure ceric solution	694.8,693.1,
With thorium	708,697
With lanthanum	665.1,658.1

Here again, the influence of the cognate metal seems unmistakable and distinctive. My only explanation lies in the complexity of the base, although I admit that the evidence, so far, is not conclusive.



## **APPENDIX**



# LABORATORY MANUAL<sup>1</sup>

## LIST OF APPARATUS FURNISHED FOR THIS COURSE

1 Notebook,	1 Bent ignition tube,
1 Manual,	2 Glass rods,
1 Pipestem triangle,	1 Meter glass tubing,
1 File,	2 Watch-glasses,
1 Horn spatula,	2 Rubber stoppers,
1 Steel forceps,	2 Cardboard boxes,
1 Test-tube holder,	1 Package filters,
1 Test-tube brush,	10 cm. black rubber tube,
1 Wire gauze,	1 10 cm. graduated cylinder,
1 Porcelain dish,	1 Box of weights,
1 Porcelain crucible,	1 Pair of scales,
1 Porcelain lid,	1 Towel.
1 Glass U-tube,	
1 Bunsen burner,	12 Test-tubes,
1 Hose for same,	2 Funnels,
1 Star for same,	1 Long-stemmed funnel,
1 Chimney for same,	1 200 cc. flask,
1 Wing-top for same,	1 750 cc. flask,
2 Iron rods,	1 Set wash-bottle fittings,
2 Iron rings,	3 Small beakers,
1 Pneumatic trough,	2 Common bottles, small,
1 Test-tube rack,	1 Common bottle, large.

This apparatus is loaned to the student on the distinct understanding that it remains the property of the laboratory. It must not be carried away, nor put to improper uses. Each student is held responsible for the apparatus issued to him, and will be obliged to return the apparatus clean and in good condition when surrendering his desk, or pay for what is missing.

Compare the above list carefully with the apparatus in your desk. Call attention to any imperfections and satisfy yourself that nothing is missing. Do not leave any apparatus outside your drawer and cupboard, when leaving the laboratory, and see that the drawer is fastened and the cupboard locked.

When the desk is surrendered, all apparatus which is returned clean and in good condition will be credited in full; pieces which are dirty or damaged, but still fit for some use, will be credited at half price. Particular attention is called to the necessity of taking good care of the weights and balances.

## HYDROGEN

To generate this gas:— After convincing yourself that the generating apparatus does not leak, remove the cork, and put

<sup>1</sup> Prepared for students in Elementary Inorganic Chemistry at New York University.

sufficient granulated zinc into the bottle to completely cover the bottom. Replace the cork, pour enough water into the bottle to seal off the lower end of the funnel-tube. Add strong hydrochloric acid, a little at a time, and in such a manner that air-bubbles shall not be carried down with it. Whenever the evolution of the gas becomes less brisk, more acid should be added.

**CAUTION:** No flame should be allowed anywhere near a hydrogen generator until gas has been evolving briskly for at least five minutes !! Do not actually apply a flame to any portion of the apparatus, until a test, according to Exp. 1, shall have proved the absence of an explosive mixture !

**EXPERIMENT 1.** To test whether air has been entirely displaced by hydrogen: — Pour so much water into the “pneumatic trough” that the perforated shelf is well covered. Immerse a test tube until it is quite full of water; raise the closed end out of the water, and rest the tube with its opened end upon the shelf. Bring the delivery-tube of the gas generator into such a position that the escaping bubbles rise into the test-tube and displace the water contained in it. When the tube is quite full of gas, close it with your thumb and carry it to a lighted burner, not removing your thumb until the mouth of the tube is close to the flame. If the gas lights with a faint sound, and the flame works its way quietly down the tube, no air was mixed with the hydrogen in the generator; but, if the gas burns all at once, with more or less of an explosion, air was still contained in the generator at the time the sample was taken. Repeat the experiment, until a sample burns quietly.

Note that this experiment must be repeated every time that the generator is set up afresh. The small volume and the thin walls of the test-tubes make these explosions harmless, whereas a similar explosion in the generator might lead to dangerous injuries.

**Exp. 2.** To compare the density of hydrogen with that of air. Fill two test-tubes over the pneumatic trough with hydrogen: hold one, mouth up, for ten seconds, then approach the mouth to the flame; hold the other, mouth down, for ten seconds, and approach to the flame. Note and explain any difference.

**Exp. 3.** Connect the inner tube of the “osmose-apparatus” with the hydrogen generator, by means of a bit of rubber tube. The pipe-bowl will be filled with hydrogen in a little more than two minutes. Pull out the inner tube and set the open end of the outer

tube under water. Observe what happens, and ask for an oral explanation.

EXP. 4. If a test-tube is only partially filled with water, closed and inverted with its mouth under water, hydrogen being then introduced, a mixture will be formed of the air left in the tube, with the volume of hydrogen represented by the quantity of water originally placed in the tube. Fill four test-tubes one-quarter, one-third, one-half, and two-thirds, respectively, full of water; invert in pneumatic trough, displace the water with hydrogen; close with thumb, carry to flame and compare violence of explosions.

EXP. 5. Dry the end of the delivery-tube with a bit of filter-paper. Allow the gas to flow upon bits of moist litmus paper, red and blue: note whether their color is affected.

EXP. 6. Wipe a beaker clean and dry; then hold it for a minute or more over the mouth of the delivery-tube and note whether anything is deposited upon the beaker. Light the hydrogen as it issues from the tube, and again hold the beaker over the jet.

EXP. 7. Fill a small bottle with hydrogen over the pneumatic trough. Lifting the bottle, mouth down, out of the trough with your left hand, push a lighted match well up into it, holding the match by means of the steel forceps, with your right hand.

EXP. 9. Disconnect the generating apparatus, and filter its liquid contents into an evaporating dish, being careful not to fill the latter above the lip; the superfluous liquid may be thrown away and any undissolved zinc can be left in the generator, for future use. The small stove in the draught-closet is lighted, the porcelain dish set upon it and heated with a small flame until the liquid has all evaporated. As this operation takes some time, and requires little attention, it can be conducted during the progress of some of the succeeding experiments.

Write the equation which expresses the action of hydrochloric acid upon zinc.

#### OXYGEN

EXP. 10. Heat about one gram of potassium chlorate in a clean, dry test-tube, being careful not to allow the flame at any time to strike that portion of the tube which is above the substance, since

## APPENDIX

this is apt to cause the tube to break. When the salt has melted and a brisk evolution of gas is taking place, hold a glowing splinter of wood to the mouth of the tube. Heat the fluid salt until no more gas is seen to be given off, and then set aside to cool (proceeding meanwhile with Exps. 11 and 12). When the tube is quite cold, add some distilled water and warm, until a portion of the fused mass has dissolved. Filter the solution into a clean test-tube, add two drops of nitric acid and five drops of a solution of silver nitrate.

EXP. 11. Dissolve about one-fourth gram of potassium *chlorate* in distilled water and add two drops of nitric acid; then five drops of silver nitrate.

EXP. 12.—Dissolve about one-fourth gram of potassium *chloride* in distilled water and add two drops of nitric acid; then five drops of silver nitrate.

What is the behavior of potassium chlorate, and of potassium chloride, respectively, toward nitric acid? toward silver nitrate? If a precipitate forms, what must it be? What conclusion can be drawn as to the nature of the solution obtained in Exp. 10? Write the equation expressing the result of heating potassium chlorate.

EXP. 13. Clean, dry and weigh a porcelain crucible and lid. Add *about* one gram of potassium chlorate to the crucible, and reweigh exactly. The difference between the first and second weighings will give the precise amount of salt used. Set the crucible upon a pipe-stem triangle, supported on an iron ring and stand, and heat gradually with a Bunsen burner, until all the oxygen has been expelled. This can be done without any danger of loss from spattering, if the heating is conducted uniformly and slowly. When the salt is in quiet fusion, allow the crucible to cool to room temperature, then weigh. The loss of weight will indicate the quantity of oxygen driven off. How much oxygen is contained in one hundred parts of potassium chlorate?

EXP. 14. To ascertain the density of oxygen gas. The apparatus furnished for this experiment consists of a tube filled with a mixture of potassium chlorate and black oxide of manganese — for generating oxygen, — a U-tube containing strong sulphuric acid, and a delivery tube. The U-tube serves to prevent the escape of everything but oxygen. Place this apparatus, with the exception

of the delivery-tube and its stopper, upon one pan of the balance, and exactly counterpoise it with sand, poured into a beaker upon the other pan. This counterpoise must not be disturbed until the experiment has been completed. Connect the apparatus up with a delivery-tube and support it so that the heating-tube is in a slanting position, while the end of the delivery-tube dips under the mouth of a large bottle filled with water, and set inverted upon the shelf of the pneumatic trough. Gradually heat the mixture in the tube, holding the burner in your hand, and keeping the flame brushing along the tube. Once heating is commenced, it must not be interrupted until no more gas is seen to leave the delivery-tube: remove the latter, with its stopper, from the U-tube; and *then* take away the flame and allow the apparatus to grow cold. (Removing the flame before the delivery-tube was disconnected might cause water to rise back into the apparatus, owing to the contraction of the cooling gas.) When the apparatus is cold, place the same parts upon the balance pan, as before: but a certain amount of weights must be added to this pan, to bring it into equilibrium with the original counterpoise. This weight should be noted, as it represents the *mass* of oxygen which has been transferred from the tube to the bottle.

We must now proceed to measure the *volume* occupied by this mass. Note the temperature of the air near the bottle. Raise the bottle slightly from its shelf, slip a piece of smooth paper under its mouth, and invert dexterously, without spilling any of the water from the bottle. No effort need be made to retain the oxygen, as its volume is indicated by the contents of the bottle above the water level. Fill the bottle brimful from a measuring-glass, being careful to ascertain the number of cubic centimeters of water required to complete the filling, as they represent the volume of oxygen at the temperature of the room,  $t^{\circ}$ . To reduce this volume to  $0^{\circ}$ , multiply it by the fraction  $\frac{273}{273+t}$ .

Knowing the volume and the mass of the oxygen produced in this experiment, calculate the weight of one liter of oxygen gas.

#### RELATIONS OF COMBINING WEIGHTS

EXP. 15. Weigh a clean watch-glass, place about half a gram of granulated zinc upon it, and weigh accurately. The difference

between this weight and that of the empty glass is recorded as the exact weight of the zinc used. Thoroughly clean the hydrogen generator, and raise the delivery-tube in the stopper, so that its end is flush with the bottom of the stopper. With the aid of your wash-bottle rinse the zinc from the watch-glass into the generator-bottle; arrange a bottle, as usual, in the pneumatic trough; but set the gas generator in such a position that the delivery-tube is not under the receiver. Pour one drop of copper sulphate into the funnel, and then so much water that all the air is driven out of the gas-generating apparatus. Now push the end of the delivery-tube under the receiver, and pour 10–15 cc. of strong hydrochloric acid down the funnel tube, cautiously avoiding the carrying down of air bubbles. The evolution of gas will begin at once; should it slacken before the zinc has disappeared, more acid may be added. (The solution of the zinc takes time, and the succeeding experiment may be commenced at this point.) When the zinc has all been dissolved, pour enough water down the funnel to drive all remaining gas from the generator into the receiver. The volume of this gas is now measured and reduced to zero, after ascertaining its actual temperature — exactly as in Experiment 14.

A cubic centimeter of hydrogen, at zero, weighs approximately .00009 gram; what mass of hydrogen was evolved in this experiment? How many parts of zinc would displace one part of hydrogen from its combination with chlorine?

EXP. 16. Weigh a clean and dry porcelain dish as accurately as possible, add about two grams of zinc and weigh again. Pour small quantities of dilute hydrochloric acid into the dish, until the zinc is all dissolved; profuse addition of acid would result in loss of time. When the zinc has been dissolved, evaporate carefully to complete dryness on the evaporating stove, then transfer the dish to a triangle supported on a ring-stand, where it is cautiously heated until the zinc chloride has just melted, the burner being held in the hand, and the flame being allowed to play *down* upon the salt. As soon as the latter has melted, cool without delay. As soon as the dish is cool enough to handle without burning the fingers, it may be set in cold water — of course without moistening its contents — so as to reach room temperature more quickly. Its outside is at once wiped clean and dry and it is reweighed, the

gain" being held to represent the chlorine which has combined with the zinc. How much chlorine would be required for one part of zinc? How much for one part of hydrogen?

EXP. 17. Brighten a piece of magnesium ribbon, and weigh off exactly .04 grams upon a watch-glass. Place the magnesium in a beaker, and cover it with a small, short-stemmed funnel, inverted in the beaker. Fill the latter with water. Fill a eudiometer with water, cover its mouth with a bit of bibulous paper, so as to be able to invert it, and set it so that its rim rests on the funnel in the beaker, with the stem of the funnel projecting into the eudiometer. Remove as much water from the beaker as possible without exposing the open end of the eudiometer, and pour a considerable amount of strong hydrochloric acid into the beaker, allowing it to run down the walls, so as to form a layer at the bottom. It will soon work its way to the magnesium, which will quickly dissolve, the displaced hydrogen rising into the measuring tube. When the reaction is completed, the beaker is again filled brimful, the eudiometer slipped off the funnel, closed with the thumb and transferred to a tall cylinder full of water, where it is allowed to remain for some time. The barometer having been read, and the temperature of the water in the cylinder having been noted, the eudiometer is lifted until the water within it stands at the same level as that without, and the volume of enclosed hydrogen is read off on the engraved scale. The calculation of the corresponding mass will be explained orally.

EXP. 18. Weigh a porcelain crucible and lid, after cleaning and drying them. Add about .8 gram of bright magnesium ribbon, and weigh again. Set the crucible on a pipestem triangle, on a ring-stand, and heat gradually without removing the lid, excepting for a moment or two at a time to admit fresh air, and observe whether the magnesium has all been burned. Avoid the escape of a white smoke. When all the magnesium appears to have burned, remove lid and heat crucible more strongly. Cool, weigh crucible with lid and contents. The gain in weight represents oxygen. In what proportion did the two elements combine?

EXP. 19. Charge the hydrogen-generator with some zinc, and replace the delivery-tube with a bent tube leading to a U-tube con-

taining a little strong sulphuric acid. The farther end of the U-tube communicates with a hard-glass tube, by means of a connecting tube and stoppers. While the hydrogen is sweeping the air out of the generator and its connections, weigh the hard-glass tube, fill about half-full of copper oxide, and reweigh. After assuring yourself that the air has been driven out of the generator according to Exp. 1, for which purpose the delivery-tube may be temporarily connected on, put the copper oxide tube in position, supporting its free end with the aid of the ring-stand. Allow a minute for sweeping the air out of this tube, then commence to warm it gradually with a Bunsen flame. Soon steam will issue at the jet, and care must be taken to keep the whole tube beyond the oxide so warm that water may not condense and run back to crack the tube. Whence does this steam come? Observe what happens to the copper oxide. When the change is complete, allow the tube to cool without interrupting the flow of hydrogen. When cold, disconnect and reweigh. With these data, calculate the ratio in which copper and oxygen combine.

**EXP. 20.** Weigh a porcelain crucible without the lid, add about 1 gram of finely divided copper, and reweigh. Fill the crucible about a quarter full of nitric acid, cover with a watch-glass, convex side down, and heat very gently until the copper is dissolved; lift off the watch-glass and, with a wash-bottle, rinse down into the crucible the green drops that may have collected on it, and evaporate the contents of the crucible to dryness on the stove. When dry, remove with forceps to pipe-stem triangle, and heat over the free flame, cautiously at first, but more strongly toward the end, until all the green copper nitrate has been converted into black copper oxide. Cool and weigh. The gain represents the oxygen which is now combined with the original copper. Compare these two weights with one another.

#### ALKALI METALS

**EXP. 21.** Remove the kerosene from a small piece of sodium with some dry filter-paper. Drop it, in small bits, into water contained in a porcelain crucible, keeping a lid on the latter, as long as chemical action is taking place. When the sodium has disappeared, take a drop of the solution upon the end of a glass rod, and touch it to a piece of red litmus paper; then add hydrochloric acid, drop

by drop, until the liquid shows an acid reaction. Write the two equations involved. The liquid in the crucible may now be evaporated to dryness, and the product examined.

**EXP. 22.** Counterpoise a beaker upon the scales and add 25 grams of a "normal" hydrochloric acid,— one gram of which contains .0365 grams of HCl. — Warm this gently, set over a wire gauze. Meanwhile, place something more than two grams of sodium carbonate in a porcelain dish, and weigh (the weight of the empty dish being unimportant). Carefully transfer this salt, a little at a time, to the acid, by means of a horn spatula, until the liquid is faintly alkaline. Reweigh the dish to find the amount of sodium carbonate required to neutralize the acid.

**EXP. 23.** Repeat experiment 22, using potassium carbonate in place of sodium carbonate, and compare the two results.

**EXP. 24.** Pour 100 cc. of calcium hydroxide into a clean flask. Dissolve a quarter of a gram of sodium carbonate in half a test-tubeful of water, and add just enough of this solution to the flask to complete the precipitation. When a drop produces no further precipitate, add a few drops of the calcium hydroxide; filter and neutralize the filtrate with hydrochloric acid, noticing whether there is any effervescence. Pour a few drops of acid upon the precipitate on the filter and note the result.

**EXP. 25.** Weigh a clean porcelain crucible. Add one gram of potassium chloride and reweigh. Add 5 to 6 cc. of dilute sulphuric acid. Heat gradually in fume-closet until dry; allow the crucible to cool, and moisten the contents with a little more sulphuric acid; evaporate to dryness. Remove crucible to pipe-stem triangle supported on ring-stand and heat with Bunsen burner, but not sufficiently to melt the salt. Cool and weigh. The crucible now contains acid potassium sulphate,  $\text{KHSO}_4$ .

**EXP. 26.** Mix on a piece of filter paper about two grams of solid ammonium chloride with about three grams of powdered calcium oxide. Pour the mixture into a specimen tube and close the latter with a perforated stopper, through which passes a straight glass tube. Over this tube slip an inverted test-tube, to the mouth of which a piece of moistened red litmus paper has been made to

adhere. Hold the specimen tube in a wire support, and heat the solid mixture gently; ammonia will be given off, as can be recognized by the litmus paper. When the test-tube appears to be well filled with the gas, remove it from the generating apparatus and hold its open end under the surface of some water contained in a beaker.

EXP. 27. Place a few cubic centimeters of ammonium chloride solution in an evaporating dish, add 4 to 5 drops of potassium hydroxide. Test the mixture with litmus paper. Now warm, holding pieces of moistened red litmus paper above the surface of the liquid until no more alkaline gas is given off. Test the solution with red litmus paper.

EXP. 28. Place a little dry ammonium chloride in the bottom of a dry test-tube and warm until the salt has volatilized. It will be observed to condense into crystals upon the cold walls of the test-tube. This is called "sublimation."

#### CALCIUM GROUP

EXP. 29. Weigh a clean porcelain crucible; add about one gram of calcium carbonate, weigh again. Heat on pipe-stem triangle gradually, using chimney on burner, for about fifteen minutes. Cool, weigh. The loss represents carbon dioxide. Pour some water on the residue, and note behavior. Test with litmus paper.

EXP. 30. Half fill a test-tube with calcium hydroxide solution. Pass in carbon dioxide by means of a clean glass tube until the precipitate which has first formed re-dissolves. Write two equations to express what has taken place. The solution that you obtained is to be divided into three parts and used in the three succeeding experiments.

EXP. 31. To one-third of the above solution add calcium hydroxide solution.

EXP. 32. Dilute another portion to ten times its volume with distilled water, in a flask. Add twenty drops of soap solution and shake vigorously.

EXP. 33. The last portion is to be boiled, filtered into a perfectly clean flask, diluted to ten times its volume with distilled water. Add twenty drops of soap solution, and shake vigorously.

EXP. 34. Weigh about a gram of gypsum carefully in a porcelain crucible, heat strongly, cool and reweigh. Heat a second time, to see whether a second loss of weight occurs. This loss of weight is due to the driving off of water of crystallization. How much water was present in the natural gypsum? Shake the residue into a watch-glass, stir up with a few drops of water, and observe the result.

EXP. 35. Prepare three test-tubes containing calcium chloride, strontium chloride, and barium chloride, respectively, each diluted with about four times their volume of water. To these three test tubes add equal quantities of calcium sulphate solutions (about 25 drops for each). Observe and discuss results.

#### ZINC, CADMIUM, AND MAGNESIUM

Hydrogen sulphide, which is used in this exercise, may be obtained from taps in the room set apart for the purpose. The student must affix his own glass tube to the rubber hose set on these taps. As the number of outlets is limited, considerable time will be saved if the students will prepare the solutions required for the following four experiments at one time, and carry the test tubes on a rack into the sulphuretted hydrogen room. If the gas is passed into the test tubes in the prescribed order, the glass delivery tube need not be cleansed between the experiments. It should finally be cleaned with a little strong acid.

EXP. 36. Dilute about 5 cc. of zinc chloride with an equal amount of water. If the solution is *acid*, neutralize as nearly as possible with ammonium hydroxide. Treat with hydrogen sulphide.

EXP. 37. Acidify a similar solution of zinc chloride with hydrochloric acid and treat with hydrogen sulphide.

EXP. 38. Dilute about 5 cc. of cadmium chloride solution to one-half its original strength. Acidify with hydrochloric acid and treat with hydrogen sulphide.

EXP. 39. Mix approximately equal volumes of the solutions of zinc and cadmium chlorides. Dilute somewhat, acidify with hydrochloric acid and pass hydrogen sulphide into the mixture until no more precipitate forms. Separate the precipitate from the solution by filtration, allowing the liquid to run into an evaporating dish. Set the latter upon the evaporating stove in your fume closet and concentrate to dryness. Meanwhile wash the precipitate once

with distilled water. Perforate the filter with a sharpened match-stick, rinse its contents into a test-tube with the aid of a wash bottle. Allow the solid to settle and pour off as much as possible of the water. Add 5 cc. of hydrochloric acid. Warm until the precipitate has dissolved. Boil for 4 or 5 minutes. Nearly neutralize with ammonium hydroxide and add ammonium carbonate.

The concentrated filtrate is poured from the evaporating dish into a test-tube, diluted, rendered alkaline with ammonia and treated with hydrogen sulphide.

EXP. 40. To a solution of magnesium sulphate add ammonium hydroxide solution.

EXP. 41. To 5 cc. of magnesium sulphate solution add 5 cc. of ammonium chloride solution, then add ammonium hydroxide solution.

EXP. 42. To the solution obtained in the last experiment, add hydrogen sodium phosphate solution.

#### ALUMINUM

EXP. 43. Dilute a little aluminum sulphate solution and add an excess of ammonium hydroxide solution.

EXP. 44. Prepare, in separate test-tubes, very dilute solutions of potassium hydroxide and of sulphuric acid, and study their action upon aluminum sulphate, as follows:—

Dilute 10 cc. of the aluminum sulphate solution with an equal bulk of water and add potassium hydroxide, drop by drop, until a precipitate, which forms at first, disappears upon shaking the test-tube. Divide the solution into equal halves (*a*) and (*b*). Acidify portion (*a*) with dilute sulphuric acid, drop by drop, until the precipitate, which forms at first, again disappears. Reunite portions (*a*) and (*b*). Write five equations expressing the various reactions that have taken place.

EXP. 45. Mix, upon a watch-glass, concentrated aluminum sulphate solution with concentrated potassium sulphate solution.

EXP. 46. Throw a little aluminum foil into a test-tube containing some strong hydrochloric acid.

EXP. 47. Throw some aluminum foil into a test tube containing some strong potassium hydroxide solution and warm gently.

EXP. 48. Hang two strips of cotton, one of which has been soaking in a solution of aluminum acetate, over a glass rod, and suspend them in a solution of logwood for five minutes. Remove them to a beaker and wash with plenty of water. Observe whether the dye adheres more firmly to one sample than to the other.

### MERCURY

NOTE. As mercury and its compounds corrode lead pipes, the slops must be thrown into jars specially provided, and not into the sink.

EXP. 49. Place about 5 cc. of mercurous nitrate solution in a test-tube, and dilute with an equal amount of water, then add potassium hydroxide.

EXP. 50. Dilute 5 cc. of mercuric nitrate solution with an equal quantity of water and add potassium hydroxide.

EXP. 51. Add hydrochloric acid to mercurous nitrate solution.

EXP. 52. Add hydrochloric acid to mercuric nitrate solution.

EXP. 53. Add stannous chloride solution, drop by drop, to a test-tube half filled with mercuric chloride solution.

EXP. 54. Allow a drop of mercurous nitrate to remain for a few moments on a clean copper surface, rinse the copper in a little water, wipe dry with filter-paper, then heat in flame.

### TIN AND LEAD

EXP. 55. Allow hydrogen sulphide gas to act on stannous chloride.

EXP. 56. Allow hydrogen sulphide gas to act on stannic chloride.

EXP. 57. Drop some tinfoil into a test-tube with hydrochloric acid and observe effect in cold and heat.

EXP. 58. Place tin-foil in a crucible, set the latter inside the fume-closet and add strong nitric acid.

EXP. 59. Treat some litharge ( $PbO$ ) with dilute nitric acid until dissolved. Test a portion of the solution with hydrochloric acid.

EXP. 60. Place a few grams of "red lead" in a test-tube, half fill the latter with cold dilute nitric acid and shake. Filter the solution from the brown residue, and test the former with a few drops of hydrochloric acid. What has gone into solution? What is the brown residue? What can we conclude as to the nature of "red lead"?

EXP. 61. Add hydrochloric acid to 10 cc. of lead acetate solution, in a test-tube, as long as a precipitate continues to form. Allow the latter to settle, pour off the clear liquid, shake the precipitate with about 10 cc. of fresh water, allow to settle and pour off water. Repeat this washing and then half fill the test-tube with water, heat to boiling and filter, if necessary, into a clean test-tube. It is well to have the filter ready in advance, as the liquid must be filtered boiling hot. Cool the clear filtrate by running water over the outside of the test-tube.

EXP. 62. Precipitate 10 cc. of lead acetate with potassium iodide and proceed as in Exp. 61.

#### CHROMIUM AND MANGANESE

EXP. 63. Render chromium sulphate solution alkaline with potassium hydroxide.

EXP. 64. Acidify chromium sulphate solution, and note whether hydrogen sulphide gas affects it.

EXP. 65. Acidify some potassium chromate solution, pass in hydrogen sulphide until the test-tube smells strongly of the gas, filter and add potassium hydroxide to the filtrate.

EXP. 66. Add sulphuric acid to 15 cc. of potassium chromate solution in a dish until the color has changed completely. Evaporate until crystals commence to form. Then set aside to cool.

EXP. 67. Add potassium chromate to lead acetate.

EXP. 68. Mix a little manganese dioxide with sodium carbonate powder on a porcelain crucible-lid. Set on a pipe-stem triangle and heat until the mass is fused. Cool, set in a beaker, dis-

solve the melt in water, add sulphuric acid. Note any changes of color.

EXP. 69. Dilute 1 cc. of stannous chloride in a beaker with 25 cc. of water; add 5 cc. of hydrochloric acid. Stir, and add potassium permanganate solution drop by drop. What is taking place?

#### IRON

EXP. 70. Add ammonium hydroxide to ferrous sulphate solution.

EXP. 71. Add ammonium hydroxide to ferric chloride solution.

EXP. 72. Add 2 cc. dilute sulphuric acid to 5 cc. of ferrous sulphate solution, then 10 drops of nitric acid, and heat. Observe that the solution becomes almost black and suddenly clears, giving off red fumes. Add a couple of drops of nitric acid and continue doing this until no more red fumes appear. Cool and render alkaline with ammonium hydroxide.

EXP. 73. Add some hydrochloric acid and a little metallic iron to 10 cc. of ferric chloride solution. As soon as this solution has become colorless, filter into a fresh test-tube, and add ammonium hydroxide.

EXP. 74. Add stannous chloride to ferric chloride, until colorless, and then make alkaline with potassium hydroxide.

EXP. 75. Dilute a little ferrous sulphate in a beaker with water, add a few drops of sulphuric acid, and then potassium permanganate, drop by drop.

EXP. 76. Add potassium ferrocyanide to ferrous sulphate.

EXP. 77. Add potassium ferrocyanide to ferric chloride.

EXP. 78. Add potassium ferricyanide to ferrous sulphate.

EXP. 79. Add potassium ferricyanide to ferric chloride.

EXP. 80. Add potassium sulphocyanate to ferrous sulphate.

EXP. 81. Add potassium sulphocyanate to ferric chloride.

## COPPER

EXP. 82. Test the action of hydrochloric, nitric and hot sulphuric acids on copper, noting the fumes that are given off in each case.

EXP. 83. Dilute 5 cc. of copper sulphate solution with an equal quantity of water. Add small bits of iron and heat. What changes take place?

EXP. 84. Add potassium hydroxide to copper sulphate solution until it is strongly alkaline.

EXP. 85. Add ammonium hydroxide to copper sulphate drop by drop, amid constant shaking, until the solution is alkaline.

EXP. 86. Weigh out .4 gram of crystallized copper sulphate (which contains about .1 gram of copper), and dissolve in 9.6 cc. of water. Measure 1 cc. of this solution into a test-tube and mix with 9 cc. of water. To a portion of this diluted solution add a few drops of ammonium hydroxide; of the remainder, measure 1 cc. into a fresh test-tube and mix with 9 cc. of water. Test a portion of this more dilute mixture with ammonium hydroxide, and proceed as before, always preparing a solution one-tenth as strong as the preceding one, until a drop of ammonium hydroxide fails to produce a noticeable coloration. Calculate the amount of copper per cubic centimeter that is required to give a visible reaction with the ammonium hydroxide.

EXP. 87. Add potassium ferrocyanide to dilute copper sulphate solution.

EXP. 88. Weigh a crucible; add about two grams of crystallized copper sulphate; weigh again. Heat carefully until the salt is quite white; cool, and reweigh. How much water did the crystals contain? Add a drop of water to the white residue.

## SILVER

EXP. 89. Add hydrochloric acid, little by little, to 5 cc. of silver nitrate until no more precipitate is formed. Throw the precipitate upon a filter and wash. Then open out the filter and

expose the precipitate to the daylight in such a manner that a portion is covered by something opaque. Examine from time to time.

**EXP. 90.** Add enough hydrochloric acid to silver nitrate solution to effect complete precipitation. Add an excess of ammonium hydroxide, and shake vigorously. Acidify with nitric acid; add more ammonium hydroxide.

**EXP. 91.** Add hydrochloric acid to 5 cc. of silver nitrate solution; allow the precipitate to settle; pour off the clear liquid; add water to wash the precipitate; pour off the wash-water. Shake the precipitate with a solution of sodium thiosulphate.

**EXP. 92.** Clean a test-tube very thoroughly by heating nitric acid in it. Pour away the acid and introduce 5 cc. of silver nitrate solution. Add ammonium hydroxide until the precipitate which formed at first is redissolved. Add a few cc. of grape sugar solution and warm gently until the silver is deposited. Pour the liquid away, and examine the color of the silver by transmitted light.

#### LABORATORY MAXIMS

There is no such phrase as "clean enough."

Never scrub off to-morrow what you can dissolve to-day.

Towels are used for drying, not for rubbing off dirt.

Neighbors' eyes were not meant for targets, nor their noses for fume-receptacles.

Glass and porcelain are not able to stand sudden changes of temperature.

Weights and hot crucibles should not be held in the fingers.

Note-books have good memories; jottings on loose paper are useful when you can find them.

An unrecorded experiment was never begun.

Chemical equations explain reactions, but do not describe them.

Too much of a reagent is as bad as too little; and the latter fault can be remedied.

Repairing damages takes much longer than avoiding them.

The following series of lecture experiments, taken from the notes of one of Professor Loeb's lectures on physical chemistry, may find a fitting place here, at the close of the elementary experiments. The outcome illustrates the point of view taken by the first paper (pages 1 to 20) of this volume.

[EDITOR.]

I DESIRE to show you a series of experiments devised by Professor Landolt, of Berlin, illustrating a class of phenomena that are grouped together under the name of Speeds of Reaction. In this particular case we shall examine the rapidity with which a reaction takes place between iodic acid and sulphurous acid. In the first place, the sulphurous acid serves to reduce the iodic acid to hydriodic acid, which as soon as the sulphurous acid is exhausted will react with any remnant of the iodic acid, producing water and free iodine. Up to the moment that the last particle of sulphurous acid has disappeared, or rather, been converted into sulphuric acid, it is impossible that iodine should be separated in the free state; consequently the appearance of this free iodine will be an indication of the time it takes for the completion of the reaction between the original substances. If this reaction were instantaneous, the appearance of iodine would immediately follow the mixing of the two solutions; but you will soon see that this is not the case. Time is necessary for the molecular exchange, and in this case, the interval is sufficiently great to be readily measured by means of an ordinary watch.

In order to enable you to detect the iodine the moment it is set free, I shall mix with the solution a little starch paste, which, as you well know, gives a blue color with free iodine. Perhaps, however, I had better show you this in the first place. I take here some starch paste in three beakers; to the first I add some iodic acid, to the second some hydriodic acid and to the third a solution containing a little free iodine. You see that only the third beaker shows a decided blue color; iodine in combination not affecting the starch in this way.

We are now ready to begin with the experiment on speed of reaction. In the first place, I measure out 25 cc. of iodic acid solution in one beaker and 25 cc. of sulphuric acid into another. The iodic acid solution being slightly stronger, we shall have a little excess of this reagent, to which I add 5 cc. of starch paste solution and 20 cc. of water. I shall now mix the two solu-

tions rapidly and note the time which elapses until the blue color sets in.

The experiment is now to be repeated; but I take solutions which have been warmed in order that the molecules may move more rapidly. The relative quantities of the total volume remain the same. You note how much more rapidly the molecular exchange has taken place.

In order now to show you that space has something to do with this reaction, I must increase the distances between the molecules in order that they shall be obliged to traverse more than the previous distance in order that they may meet one another. How can I do this? Simply by distributing them evenly over a larger amount of water. You will remember that I had employed 25 cc. of each acid solution, 5 cc. of starch paste and 20 cc. of water, or 75 cc. in all. If I now preserve all of these measures, excepting that I substitute 95 cc. of water for the 20, the total bulk will be 150 cc., while the molecules of reacting acids will remain the same. In this case, then, the speed is very much diminished, although the time required is not exactly doubled, for there are so many other questions entering in here, — the reaction is complicated.

In order to produce still another effect, I shall maintain the quantities of this last experiment, but raise the temperature. The time now approximates that of the first experiment.

Yet another variation may be easily made; I shall increase the amount of iodic acid while maintaining the amount of sulphurous acid, and I shall again so arrange that the total volume is 75 cc. A little explanation is here necessary, inasmuch as I shall take only 25 cc. of iodic acid solution, but this is made of just double the strength of the one I originally used. In this case, again, you will see the speed of reaction is augmented and the time very much reduced.

The results that I have shown you here involve energy, space, and time, as well as matter, and I have varied the energy by changing the temperature, and the space by changing the volume, and you have seen how time was affected.

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